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COLLOID CHEMISTRY

THEORETICAL AND APPLIED

BY SELECTED INTERNATIONAL CONTRIBUTORS

COLLECTED AND EDITED BY
JEROME ALEXANDER

VOLUME I
THEORY AND METHODS

BOOK DEPARTMENT
The CHEMICAL CATALOG COMPANY, *Inc.*
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Preface

All human activity may be resolved into two categories: we can sense and think, and we can change the position of matter. Everything else follows as the consequence of the working of inexorable laws—the so-called Laws of Nature.

Thought, deliberation, and judgment precede our conscious activities which set natural laws into operation; and if we would unerringly have a certain resultant, we must understand and foresee every relevant consequence of our shifting about of material things. We must, therefore, know material things and the natural laws which govern them.

But mere scattered, jumbled, and disorganized knowledge cannot well aid deliberation and judgment. We need *Science,* which, as Herbert Spencer has said, is *classified knowledge.*

Besides its usefulness, there is a nobility in the classified knowledge we call Science. In the Bible (Proverbs *25,* 2) it is stated:

"It is the glory of God to conceal a thing: but the honor of kings is to search out a matter."

And Virgil (Georgicon II, 490) says:

"Felix qui potuit rerum cognoscere causas."

The degree of civilization of a people is commensurate with the extent to which they accumulate, correlate, and utilize knowledge.

Nature, as an ancient Chinese saying beautifully puts it, is an inexhaustible treasure-house. Year after year the fields and forests, the mines and the seas, give us their lavish yield. But the scientific investigator not only continues to work old territory, but also opens up, from time to time, new and unsuspected areas, such as X-rays, wireless waves, radio-activity, relativity, and sub-atomic phenomena.

Just as we have had surprising developments in the fields of neglected vibrations and neglected corpuscles, so too the field of neglected dimensions, as Wolfgang Ostwald once termed the zone of colloidal dispersion, has yielded and continues to yield knowledge, which besides being important in itself, enables us the better to appraise, classify, and utilize much of our older information.

The modern tendency towards specialization has its advantages and its dangers. Naturally, intensive study in one field, or even in a restricted portion of a field, enables the investigator to develop new facts and relations which could not ordinarily be seen with less sustained effort. But unless he has been able to keep *en liaison* with other branches of science, the investigator will not be able to appreciate the full significance of his findings. Thus cytologists, intent upon morphology, often fail to see the underlying physico-chemical principles which seem to be involved in cell division, for example.

In large research organizations, this deficiency in breadth of view is met by assembling specialists, who attack common problems in collaboration. Our hospitals, medical research laboratories, and even our technological research laboratories, tend to become groups of specialists. However, even these organizations must have heads who are not administrators merely, but leaders

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and directors capable of understanding and advising with their colleagues. And the demand for the general practitioner or family physician can never be met by medical specialists alone.

Common results of lop-sided training are narrowness, smug self-satisfaction, and a lack of that humility which should keep our minds ever receptive to new ideas and new points of view. Mentally, we should grow expansively, like the chambered nautilus. We should approach the study of natural phenomena with a realization that they generally involve the simultaneous action of a number of natural laws, one or more of which may become dominant as conditions vary, thus leading to a deceptive appearance of simplicity. *It is we who are simple, not Nature.*

This book had its inception in the fall of 1922, when Mr. Francis M. Turner, Jr., Technical Editor of the Chemical Catalog Co., asked me to prepare a comprehensive book on colloid chemistry. Realizing that it would not be possible to prepare a satisfactory book single-handed, I suggested making the book an international one, and set out to obtain the cooperation of competent men in all countries. The response to this effort showed clearly the international brotherhood of science, for over 175 papers were promised by contributors from all over the world; and although death and unforeseen circumstances made impossible the delivery of some of the papers, the major portion has already been received.

The fact that contributions have been received from representatives of so many races, nations, and nationalities, indicates the unifying effect of Science, which combines men of the most diverse characteristics in a common effort to seek out the truth and to serve mankind.

As the papers began to come in, it became evident that the book would divide itself naturally into three parts: I, *Theory and Method;* II, *Biology and Medicine;* III, *Technology.* Consequently effort was concentrated on securing all papers belonging to Volume I, and getting them ready for publication. Volume I, presented now, contains practically all the papers originally promised, and quite a few others besides. The subsequent volumes will appear as rapidly as possible after the papers for them have been received.

Not only has no effort been made to select contributors whose ideas and opinions agree on all points, but on the contrary, the proponents and exponents of diverse and even conflicting views, have been asked to state their ideas freely and without reserve. In many cases the Editor does not agree with the views expressed, and may take occasion, in foot-notes or in independent paragraphs, to indicate his own or other dissenting opinions. On the evidence and arguments thus presented on many moot questions, the reader will exercise his own judgment.

Although this method of presenting diverse views will be less satisfying to some than the dogmatic statements so often found in texts unaccompanied by even a suggestion that there are conflicting views and evidence, it will lead us nearer the truth and tend toward a further extension of our knowledge. For several generations Prout's hypothesis as to the fundamental nature of the hydrogen atom, was held up as a typical example of a theory disproved by careful research, though recent work has shown it to be basically sound.

Fortunately most chemists and physicists possess flexibility of mind, so that hardly even in localized spots in these sciences do we see in operation the principle that where growth ceases, decay begins.

Throughout the books, due acknowledgment and credit will be given those who have contributed papers or translated them. Besides these, many other friends have aided with advice, reprints, proof-reading, and the like. Each contributor has read proof of his own paper, so that the book is fairly well up to date. The spirit actuating the contributors, translators and other helpers is evidenced by the fact that not one of them has been promised any definite pecuniary recompense, and that many have requested that any honorarium which might be apportioned to them, be distributed among others.

As far as possible, the contributions are arranged into more or less coherent groups, so that while each paper is an entity in itself, their interrelations lead us over practically the entire field. There is naturally some overlapping, but this has been met by condensation rather than by elimination. It is often stimulating to hear similar and even identical ideas differently supported and expressed.

While the Editor will, so far as his knowledge goes, see that justice is done, no attempt will be made here to pass upon disputed questions of priority, should these arise. On the other hand, the Editor will welcome corrections or suggestions, which might be of value for use in the subsequent volumes or editions.

Jerome Alexander.

May 1st 1926

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The Sub-Microscopic Structure of Matter

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Philosophy teaches us that we can never expect to form even a mental picture of the ultimate material unit, or of the universe, since both are indefinite. The smallest particle we can imagine must be conceived of as having a front and back, right and left, top and bottom, that is, as being divisible; and imagination cannot carry us so far that we cannot still conceive of a something beyond.[*] But here, even within the range of our limited senses, reinforced, extended and refined by instruments, we find ever-enlarging worlds of wonder.

Protons and Electrons

The smallest material units whose existence as separate entities has thus far been experimentally demonstrated, are protons,[†] the individual particles of positive electricity, which, when combined with electrons, or individual particles of negative electricity, make the various complexes we know as chemical elements. Though too small to be seen, Millikan measured the electron by catching it on ultramicroscopically visible oil or mercury droplets. Its charge is 4.774×10^{-10} electrostatic units, a figure which may best be comprehended by Millikan's statement that the number of electrons passing in a single second through an ordinary incandescent bulb is so great, that it would take 2½ million people, counting continuously day and night at the rate of two a second, about 20,000 years to complete the task. Present evidence indicates that the proton or positive electron is smaller than the electron, but much greater in mass.

Atoms

A further idea of the minuteness of the electron is given by Rutherford's and Bohr's comparison of chemical atoms to miniature solar systems, wherein the central "suns" or nuclei (complexes of electrons and protons with a net positive charge) are surrounded by planetary electrons whose relative remoteness from the nuclei is so great in proportion to their diameters, as to justify this comparison.

It is especially interesting to note that the chemical behavior of an atom is dependent upon its exterior layer or ring of electrons, the nature of which is, in turn, determined by the net positive charge of the nucleus, wherein is concentrated almost the entire mass of the atom.[‡] Since in many cases, nuclei having different structures may, nevertheless, have the same net positive charge, we are confronted by the surprising fact that the atoms of elements are not necessarily all alike. Indeed the work of Aston, Rutherford, Harkins and others has demonstrated, e.g., that there are two kinds or isotopes of lithium (atomic weights 6 and 7), two isotopes of chlorine (atomic weights 35 and 37, the usual mixture averaging 35.5), and six isotopes of mercury.

---

[*] As Herbert Spencer expresses it ("First Principles"), the ultimates of both Science and of Religion are unthinkable. Chapter IV deals with the Relativity of All Knowledge, so that Spencer was, so to say, a philosophical precursor of A. Einstein.

[†] Millikan prefers to call these positive electrons ("The Electron").

[‡] If an atomic nucleus loses a constituent electron or proton, its net charge and chemically characteristic electron rings change, and it becomes another element. This transmutation has been effected experimentally by Rutherford.

Atoms, then, are highly complex units, and in the present state of our knowledge may be classed as *complexities of the first order.*

MOLECULES

The combination of atoms to form molecules is the especial field of the chemist. The number of compounds is enormous and ever increasing. Being composed of atoms, molecules are obviously larger and more complex than their component atoms. They may therefore be termed *complexities of the second order.*

The X-ray spectrometer of Bragg reveals the fact that in crystals of sodium chloride, for instance, the atoms of sodium and of chlorine are regularly arranged in the space lattice so that each atom of sodium (on the interior) is surrounded by six atoms of chlorine, each 5.56 Å. U.[*] from it. This means that the chlorine atoms are similarly situated, and gives, in cases like this, some color to the view of I. Langmuir that a crystal is in effect one large molecule. It is quite evident that in dealing with masses of matter, the formulæ of the chemist represent rather hypothetical units, which often enjoy only a momentary separate existence, and in some cases not even that.

MOLECULAR GROUPS

The position of surface atoms, molecules or molecular groups is anomalous owing to their contact with a phase of different chemical composition; and the smaller the masses, the more marked do the effects of this anomaly become. Furthermore, the formation of perfect crystals, though generally a possibility, is often inhibited. The residual attractive forces (residual valences or free fields of force) frequently express themselves by forming relatively small molecular groups, whose size and duration of life are the result of a lag in kinetic equilibrium depending on temperature, pressure, the presence of nuclei, of impurities, etc. Associated liquids are well known, ordinary water being mainly dihydrol $(H_2O)_2$, with some trihydrol $(H_2O)_3$.[†]

In some cases the molecular union becomes *irreversible* under ordinary conditions, and we have polymerization, with the formation of new and larger molecules, which in their turn may undergo aggregation. The formation of solids from liquids may in general be considered as an aggregation of molecules, tending toward the formation of very regularly oriented groups, but not always reaching the objective. Interference due to great increase in viscosity following sudden chilling, or to the presence of slow-moving groups of large surface which adsorb or are adsorbed,[‡] may cause the solid to have a more or less finely integrated structure.

Molecular groups may be considered as *complexities of the third order.*

---

[*] 1 Å. U. (Ångstrom Unit) $= \frac{1}{10}\ \mu\mu = \frac{1}{10,000,000}$ mm.

[†] See paper by W. E. F. Turner, this volume.

[‡] Protection; or where the groups consist of the same substance, auto-protection, leading to isocolloidism. See paper on Protection by J. Alexander, this volume.

Primary and Secondary Colloidal Particles

The physical size of molecular groups must depend upon the kind and number of their component molecules. Some molecules are themselves so large that they approach or enter the limits of ultramicroscopic visibility—thus the molecule of soluble starch is supposed to be about 5 $\mu\mu$ in diameter. G. A. Hulett has shown that the tendency is for the larger particles to grow at the expense of smaller ones; but on the other hand T. W. Richards[1] has pointed out the enormously greater speed of the incipient stages of crystallization, which over a certain period makes for the separate existence of discrete groups. There is much reliable evidence for believing that a globulitic (G. Quincke, O. Lehmann) or a colloidal (P. P. von Weimarn, J. Alexander) stage is a precursor of crystallization, and that these preliminary molecular groups often remain together without fusing into larger units; just like the droplets of an oil emulsion, where coalescence may later occur when the films about the droplets give way.* Zsigmondy terms such primary colloidal particles *"protones."*

Primary colloidal particles of this nature are *complexities of the fourth order.* Their internal structure, which permits of the adsorption of other substances, ions, etc., is of such dimensions that it has become a factor to be reckoned with; for they may swell or shrink. As T. W. Richards has shown, even atoms themselves must be regarded as compressible.

In some cases these primary colloidal particles may form groups in which they still maintain their individual identity (W. Mecklenburg; R. Zsigmondy term them "polyones"), although they are bound together by forces of diminished potency. *Secondary colloidal particles* of this character are *complexities of the fifth order.* They may, by not too drastic treatment, be broken up into their constituent primary groups, and be later regenerated. Their swelling is a more complicated process than that of primary colloidal particles, for their interspaces are larger and interfacial forces less powerful. The swelling of the primary colloidal particles themselves, as well as their separation, may also be a factor in the swelling of secondary colloidal particles. Gelatin[2] evinces a duplex structure of this character; its aggregation processes are largely reversible if its solutions are not heated too high or too long.

Microscopically Resolvable Particles

All the material units we have thus far considered are below the limit of microscopic *resolvability;* for since they are smaller than a wave length of light, we cannot see various points of their perimeter. But they may be made *individually visible* against a dark background (ultramicroscope), providing they reflect or diffract sufficient light and do not move too fast. In like manner the most powerful telescope is unable to resolve even the nearest star; but a good field glass will resolve the planet Venus, and the sun and the moon are resolved by the unaided eye.

In cases *where microscopically visible particles* result from the union of secondary colloidal particles, they are *complexities of the sixth order.*

Macroscopic Particles

From what has been stated above it is obvious that in some cases ordinary *macroscopic particles,* visible to the naked eye, may be *complexities of the seventh order.*

---

* Droplets of fat, floating on clear soup exhibit this phenomenon; also fat in a cream layer. Ultramicrons of sulphur form globulites, this formation being evidently due to surface forces.

TABLE I

Material Unit	Order of Complexity	Approximate Size Limits	
Proton *	**0?**	3×10^{-12} mm. 3×10^{-6} μμ 3×10^{-5} Å. U.	
Electron †	0?	3×10^{-12} mm. 3×10^{-6} μμ 3×10^{-5} Å. U.	Atomic nuclei—Light atoms, about 5×10^{-5} Å. U. Gold, about 3×10^{-4} Å. U. (Rutherford.)
Atoms	1	0.1–0.6 μμ 1–6 Å. U.	Shortest known X-rays—0.0057 μμ (0.057 Å. U.). Dia. H atom—1.08 Å. U, (Bohr). Smallest distance between C atoms in diamond—1.53 Å. U. X-ray data of crystal units. Ni—2.76 Å. U. Fe—2.86 Å. U. Na—4.30 Å. U. NaCl—5.56 Å. U. Ultramicroscopic limits—about 2 μμ
Molecules	2	0.2–5 μμ	
Molecular groups	3	0.5–10 μμ	Amplitude of Brownian motion of Pt hydrosol at 19° C. Av. particle size = 25 μμ. = 2100 μμ in 0.0065 sec. (323 μ per sec.).
Primary colloidal particles	4	2–20 μμ	Connecting zone between shortest ultraviolet and longest X-rays 60-8 μμ.
Secondary colloidal particles	5	5–100 μμ	Average Free Paths: CO_2 = 61.5 μμ NH_3 = 66.0 N = 92.9 O = 99.3 H = 160.0 He = 300.0
Microscopically resolvable particles	6	Over 250 μμ	Microscopic limits for resolution about 250 μμ. Visible Spectrum: Violet— about 4,000 Å. U. Blue— 4,700 Å. U. Green— 5,200 Å. U. Yellow— 5,800 Å. U. Orange— 6,000 Å. U. Red— 6,500 Å. U. Limit of visibility—8,000 Å. U.
Visible particles	7	About 20,000 μμ 2×10^{5} Å. U.	Longest infra red from Hg vapor—0.313 mm. (313,000 μμ). Shortest Hertzian waves 2.0 mm. (2,000,000 μμ).‡ Electro-magnetic vibrations of alcohol—70.0 cm. Hertzian wireless waves 100 m.—30,000 m.

N—number of molecules in 1 gram molecule = 60.62×10^{22}.

h—Planck's constant of action 655×10^{29} erg seconds.

e—charge of the electron 4.774×10^{-10} electrostatic units.

Human voice	60—12,000	vibrations per second.
Audible sound	16—30,000	" " " (human).
	60,000 ±	" " " (mice).
Mechanically detectable	90,000	" " " (Koenig).

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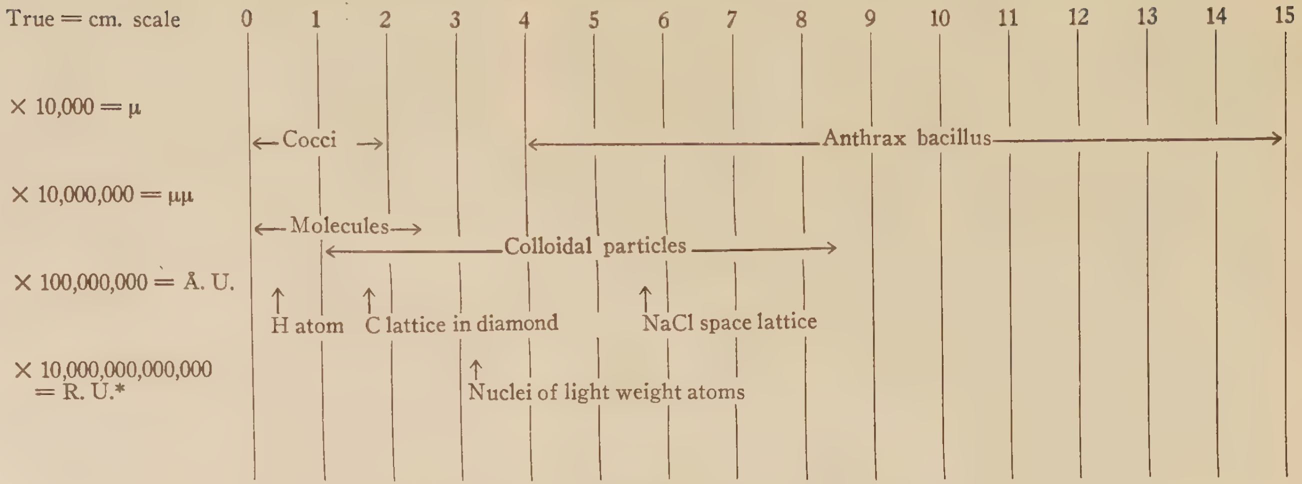
* Rutherford's estimate from experiment.

† Lorentz, from electromagnetic theory.

‡ Nichols and Tear.

Chart Showing Sizes of Various Units at Various Magnifications



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* In dealing with the extremely minute sizes involved in describing nuclear diameters, it is convenient to use a unit of measurement one million times smaller than 1 μμ. This I have termed a "Rutherford Unit" (R. U.), and therefore 1 R. U. $= \frac{1}{100,000}$ Å. U. $= \frac{1}{1,000,000}$ μμ.

Shapleigh estimates the diameter of the Milky Way at 300,000 light years or 19^{24} cm., and the size of the proton is 3×10^{13} cm. Therefore in an exponential range of 37 as applied to the centimeter, we may pass from the super-ultramicroscopic to the macroscopic limits of the Galaxy. This shows the condensation wrought by exponential notation, as with p_H.

In order to give a bird's-eye view of these units and their relationship to each other and to some other physical constants, the subjoined table has been prepared.

Diversity of Structure in Macroscopic Particles

It is not necessary that each of the foregoing steps, from protons and electrons to microscopic particles, exist in a distinguishable form in every particle of any substance visible to the naked eye. In the case of perfect crystals, of simple substances at any rate, there seems to be no easy way to distinguish between molecule and crystal. But even perfect crystals on careful ultramicroscopic examination, often show adhering colloidal groups, vestiges of the mechanism by which they were produced.

This at once suggests the idea that in a visible particle, all the constituent sub-groups need not necessarily be of the same order of size. The crystallites of the petrologist, found in pitchstone, obsidian, and other rapidly cooled volcanic rocks, are forms intermediate between colloidal aggregates and true crystals, and Quincke, H. J. P. Vogelsang and many others believe that a globulitic stage precedes visible crystal formation—the qualifying word *visible* is used because P. Scherrer found that even amicroscopic colloidal gold particles are crystalline, while in colloidal silicic acid and stannic acid random or haphazard groups are also present.

On preparing ultramicroscopic fields of slides prepared by dissolving sulphur in carbon disulphide, adding a little Canada balsam as a crystal inhibitor or protector, and rubbing out a thin film of the solution so that the solvent quickly evaporated. In the dried film the following structures could readily be identified:

1. Numerous *ultramicrons* in random arrangement.
2. *Globulites,* some with, others without apparent crystalline character.
3. *Margerites* (from Gr. μαργαριτης, a pearl), globulites arranged in bead-like strings.
4. *Globospherites,* globulites arranged in clusters.
5. *Definite crystals,* which were in every instance surrounded by a vacant space cleared of its ultramicrons by the giant ogre-like crystal which had absorbed them. Many crystals had ultramicrons or globulites adhering to their surfaces as if these had been drawn there by surface forces and had either been unable to fit into the crystal space lattice, or had been prevented from doing so because of sudden chilling, evaporation of the solvent, or interference of the protector.

This experiment was devised by Sir J. S. Flett, who, however, did not examine the results ultramicroscopically.

The Importance of the Microscopic and Ultramicroscopic Structure of Matter

Without gainsaying its importance, ultimate chemical analysis is not an end, but is simply one essential and important step toward understanding the behavior of matter. Without interpretation or further information how insufficient does the average "chemical analysis" seem to the average "practical

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[*] See "The Colloidal State in Metals and Alloys," by J. Alexander; *Colloid Symposium Monograph,* University of Wisconsin, 1923. The phenomena are quite similar to the phenomena exhibited in the illustrations in Chapter 22 by Howard T. Barnes, and Chapter 52 by Herbert W. Endres in this book.

man"? Our experience with isomerism in its different forms (metamerism, polymerism, tautomerism) has taught us that even from a purely chemical standpoint the knowledge of definite proportions of elements in a compound may often leave much more to be said. The work of Pasteur, LeBel, van't Hoff, and E. Fischer drove home the existence and the significance of stereo-isomerism, the distribution of atoms in space; and the study of reversible reactions (including reversible allotropism), hysteresis (including syneresis), and the behavior of colloidal substances, has given us evidence of the importance of that other concomitant of space—namely *time*. Many experiments fail because the supposed end-point is read too soon. Roberts-Austen laid sheets of lead and gold together, and found at the end of five years that they had sensibly diffused into each other. Colloids are essentially substances in a labile or metastable state, and the general tendency is for their interrupted aggregation processes to establish themselves, if given opportunity *and* sufficient time. Thomas Graham was right when he said that colloids possess *Energia.*

Many of the ordinary working properties and engineering qualities of matter depend upon its finer structure rather than upon its ultimate chemical analysis. The properties of two webs of cloth having the same weight of cotton per square yard depend upon the number of threads in the warp and woof, as well as upon their distribution; but in most cases the causes of differences in the behavior of substances are not so obvious.

By varying the time and temperature of heating, the point and speed of chilling, and the time and temperature of re-heating, a wide variety of practical properties may be produced in one and the same steel. Molten sulphur dropped into liquid air gives a transparent rubber-like mass, which gradually becomes brittle as its interior structure becomes crystalline.[*] The widespread use of ageing, maturing, tempering, and similar processes in the various arts and industries all bespeak the importance of securing in matter the desirable internal structure.

GASES, LIQUIDS AND SOLIDS

Although, if we peer profoundly enough, all matter has as its basic units protons and electrons, still for many practical purposes, atoms, molecules, molecular groups, primary or secondary colloidal particles, microscopic particles, or even macroscopic particles, may be the units on whose behavior we must mainly concentrate our attention in order to understand many of the ordinary physical properties of substances.

With an ideal gas the tendency is for the constituent atoms or molecules continually to rebound apart, and the existence of any temporary grouping of molecules would be in accordance with the laws of probability. With increasing pressure and decreasing temperature, the chances for the formation and persistence of groups of molecules increases, and at the critical point there appears the opalescence studied by A. Einstein [†] and others. With liquids, molecular grouping or aggregation must be much more marked than is the case with gases,[‡] and even if any *one* aggregate of molecules has but a limited period of existence, *the number of aggregates existing at any one in-*

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[*] The effect on structure and behavior of even traces of "impurities," is often startling, and may make or mar a reaction or a process.

[†] See paper by A. Einstein, this volume.

[‡] With gases, kinetic activity dominates attraction; for as O. E. Meyer says ("Kinetic Theory of Gases," § 85), "The attractive forces which are recognized by us in liquids and solids as cohesion and hardness are, according to Joule and Lord Kelvin's experiments, not absent from the molecules of gases too."

stant will be large and will approximate a mean value which varies with the liquid and with conditions.

Immobility is what most characterizes a solid from the popular point of view. This does not mean that within the solid there is no motion; for its protons, electrons, atoms and even molecules may move. Thus tin and lead anneal at ordinary temperatures. But pragmatically speaking, the constituent particles of true solids do not move with respect to each other under the force of gravity, at least not to a noticeable extent over ordinary periods of observation; and we say that the solid maintains its shape. Once the particles of an apparently solid substance begin to move with respect to each other, the substance will flow. A glass rod supported at both ends will sag, and a cork will float up through pitch if given sufficient time.

It is fair to assume that there is a continuity of the liquid and gaseous states (J. H. Jeans, "The Dynamical Theory of Gases," p. 200; see also Van der Waals, "On the Continuity of the Liquid and Gaseous State," Leyden, 1873); and that "when a gas or vapor is at a temperature which is only slightly greater than its boiling point at the pressure in question, it cannot be regarded as consisting of single molecules, but must be supposed to consist partly of single molecules and partly of clusters of two, three or more molecules." As molecular aggregation increases, the gas becomes a vapor and shows the cloudiness of the critical state, until finally the droplets join into one cohering mass, and we have a liquid. In like manner, as the constituent particles of a liquid decrease their kinetic motion, a state is reached where there is no motion, or practically none, and we have what we call a solid. While decrease in temperature decreases kinetic motion, this effect is exaggerated by the fact that this initial decrease of motion enables the specific attraction of the particles to assert itself and form larger aggregates whose motion diminishes very sharply as their size increases, until with particles of about 5 μ motion practically ceases.

Let us now consider the viscosity of gases and of liquids. We are at once struck by the fact that the viscosity of liquids *diminishes* rather rapidly with increase of temperature, while the viscosity of gases *increases* with increase of temperature, but to a much smaller extent.*[3] At first blush this might seem to be an anomaly, but on reflection it will appear that there are at least two principal tendencies of increase in temperature, and that these vary at quite different rates in gases from what they do in liquids. The first tendency of heat is to increase kinetic activity of the particles. The second tendency of heat is to *deflocculate* and thus diminish particle size.†

TABLE II

TEMPERATURE VARIATIONS OF VISCOSITY IN GASES AND IN LIQUIDS

ν for Gases			ν for Liquids		
Air	0°	0.00017	Water	0°	0.018
	20°	0.00019		20°	0.010
	100°	0.00022		100°	0.0028
O	0°	0.00019	Alcohol	0°	0.018
	20°	0.00021		20°	0.012
H	0°	0.00008		72°	0.005
	20°	0.00010	Glycerin	2.8°	42.0
CO_2	0°	0.00014		20.3°	8.30
	20°	0.00016		26.5°	4.94

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* This is shown in Table II

† This may be conceived of as being in part due to decrease in specific attraction, consequent on atomic expansion or the internal kinetics of the groups.

With a perfect gas there would be no molecular aggregation to consider, and assuming such a gas to be confined, the only effect of heat (besides molecular swelling) would be to increase the velocity of the molecules, thus bringing a larger number into closer frictional contact over any given shearing plane per unit of time, and slightly increasing the viscosity. The experiments of Thomas Graham (Phil. Trans. 1846 and 1849) on the flow of gases through tubes are in accord with the statement of Meyer (*lib. cit.* p. 85): "The increase of friction with the temperature is in nearly the same ratio for all gases . . . ; for the speed of the molecules, which comes as a factor into the formula for the coefficient of viscosity, increases with the temperature at nearly the same rate for all gases; and it is not unreasonable to expect the same also with respect to the free path." The specific molecular attractions of the gaseous molecules become dominant as their critical points are approached, and are important factors in determining liquefaction.

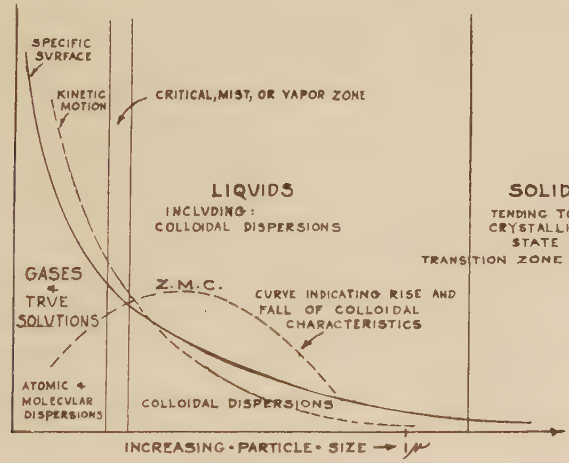
SPECIFIC SVRFACE
KINETIC MOTION
CRITICAL, MIST, OR VAPOR ZONE
LIQVIDS
INCLVDING: COLLOIDAL DISPERSIONS
SOLIDS
TENDING TO CRYSTALLINE STATE
TRANSITION ZONE
GASES + TRVE SOLVTIONS
Z.M.C.
CURVE INDICATING RISE AND FALL OF COLLOIDAL CHARACTERISTICS
ATOMIC + MOLECVLAR DISPERSIONS
COLLOIDAL DISPERSIONS
INCREASING • PARTICLE • SIZE → 1μ

Fig. 1.

The relation between the solid, liquid, and gaseous states is illustrated by the diagrammatic figure (Fig. 1), in which the curve *KM* represents the mean kinetic velocity of translation of the constituent particles, the curve *SS* represents specific surface (free or rind surface per gram), figured on the assumption that the constituent particles are spheres (which is only sometimes the fact), *V* represents rise and fall of viscosity as due solely to changes of dispersion and showing a maximum in the colloidal zone (Zone of Maximum Colloidality). The transition between the gaseous and liquid states is through the narrow mist or vapor zone which takes in the critical state. In the liquid state molecular aggregation is favored by pressure, lower temperature, specific attraction of molecules,* the removal of protectors and the presence of coagulators. As molecular groups increase in size and number, the particulate activity of the system (that is, the activity of the individual particles comprising it) diminishes; but as the relatively immobile "solid" state is approached, a considerable increase in particle size means only a small decrease in kinetic motion, so that the true solid state is reached through a broad "twilight zone" wherein apparently solid substances may show the results of their slow internal motion over long periods of time.

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* This is increased upon atomic or molecular shrinking, the exterior electrons falling into orbits nearer the nuclei.

A capital instance of what may happen in "solids," if we only wait long enough, is shown in the travertine (a calcium carbonate mineral) deposited by the Mammoth Hot Springs at Yellowstone National Park, U. S. A. Owing to its sudden release from solution due to cooling and escape of CO_2, and owing perhaps also to the protective action of the slime of the algæ growing in the hot water, the freshly deposited travertine shows a filamentous or crypto-crystalline structure. The older deposits show increasing evidences of crystallinity, until on reaching the oldest deposits at the top of the terraces, estimated by geologists to be between twenty and thirty thousand years old, good-sized sparkling crystals are found, which, however, still maintain the rhythmic rings of the original deposit.

What we commonly call the solid state is, therefore, generally a state of flux and slow internal readjustment; and there is ample justification for the view expressed by E. W. Washburn ("Physical Chemistry") that the three classic states of matter are not gaseous, liquid and solid, but gaseous, liquid and *crystalline*. Many "solids" consist of fine crystals embedded in what may just be considered a still liquid matrix, but in many cases even the major portion of the matrix may consist of tiny or ultramicroscopic crystals, and X-ray spectrographic examination will probably show that many "solid solutions," so-called, are not truly such.

The tendency of heat to diminish particle size (apart from its probable swelling action on the atoms) is of minor importance with gases because of their already highly dispersed state. With pure liquids, where the molecules are much more closely packed and have much greater cohesion than in gases, molecular groupings must be larger and more numerous. If these groups are of colloidal dimensions, the liquid is an iso-colloid, and as the groups grow at the expense of the dispersing phase, the liquid tends to go over into the solid state. In fact *every pure substance* in aggregating from molecular dispersion to visible particles (or vice versa) must of necessity pass through a zone of colloidal iso-dispersion or iso-colloidism. (See von Weimarn, this volume, p. 27.)

With liquids, therefore, heat exerts a marked dispersing action, *diminishing* the number and size of the aggregates, *with a corresponding increase* in what we might call the "dispersing phase." This is equivalent to the *simultaneous* dilution of the "dispersion" *and* reduction of the percentage of the "dispersed phase." With solids heating does not show any *visible* effect (apart from expansion) until atomic or molecular "swelling" and increased internal kinetic motion become great enough to permit particulate kinetic activity, consequent upon the lessening of the attraction of the molecules and the molecular groups for each other. The solid is then in a state of incipient fusion—it is semi-liquid, and a slight increase in temperature, or even mere agitation makes it fluid.

THE ZONE OF MAXIMUM COLLOIDALITY

As Fig. 1 indicates and practical experiment proves, it is possible to bring any substance into a colloidal degree of dispersion by either of two general types of procedure: (1) by *grinding* or *dispersing* relatively large particles; (2) by permitting molecularly dispersed particles to *aggregate* to a limited extent. Svedberg calls these *dispersion methods* and *aggregation methods* respectively.

In passing from the region of suspensions where visible kinetic or Brownian motion just begins, to molecular dispersion where kinetic motion is very violent, it is obvious that we pass from a region where specific surface (such as it is) is dominant, to a region where, notwithstanding an enormous increase in specific surface, kinetic motion is the dominant factor.

In the course of the transition from the region where specific surface is dominant to the region where kinetic motion is dominant, there must be passed a region where these two factors are nearly balanced, where increasing specific surface shows its effect *before* kinetic motion becomes sufficiently violent to reduce surface attraction factors to a level of lesser relative importance. This region is the colloidal zone of dispersion, and theoretically, colloidal properties such as viscosity, should reach their maximum where the dominance of specific surface ends and that of kinetic motion begins. This optimum zone in the colloidal region has been termed by Alexander[4] the *zone of maximum colloidality*. It was first observed experimentally, an understanding of its theoretical explanation coming later. Some practical instances will be given below, showing the occurrence of the zone of maximum colloidality. Meanwhile we might consider it mathematically.*

Purely for the sake of mathematical convenience, we will regard the individual particles whose surface and motion we are to consider, to be perfect spheres. We know in some cases, *e.g.*, V_2O_5 sols, that this is not so, but there is much evidence in other cases (*e.g.*, S sols) that it is; and the tendency of surface tension is to make particles spherical.

Now with spheres we know that their *area* varies as the *square* of the diameter, whereas the *volume* (which also means approximately the *mass*) varies as the *cube* of the diameter. That is, for one individual sphere, if d is the diameter

$$A \sim d^2$$
$$M \sim V \sim d^3$$

However, *for a unit weight (or mass)*, the *specific surface* varies inversely as the square of average diameter; that is

$$SS \sim \frac{1}{d^2}$$

And the *mean kinetic motion* of the particles in this unit mass will vary inversely as the cube of the average diameter; that is

$$KM \sim \frac{1}{d^3}$$

The reciprocals are used because mean kinetic motion and specific surface increase with *decreasing* values of d.

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* It must be very strongly emphasized that we do not yet know enough to include in any mathematical analysis all of the factors controlling the behavior of matter; and if we did we would be overwhelmed by the formulas involved. Mathematicians confess themselves unable to calculate what will happen when three bodies act upon each other according to Newton's laws of gravitation—the so-called three-body problem has never been solved. It is therefore a sort of scientific narcosis if we lull ourselves into a sense of fancied omniscience based upon "rigid mathematical analysis." See p. 17. On the other hand, mathematics is an extremely valuable tool to use in attacking problems involved in natural phenomena. However we must remember that in framing a mathematical equation, we not only depend upon the correctness of the assumptions made, but at the same time *tacitly assume that there are no factors omitted*. Therefore when experiment fails to confirm a law or equation which is correctly derived from a mathematical standpoint, it is probable our assumptions are breaking down under those particular experimental conditions, or else that we have omitted some factor which there becomes of importance. With a full realization, then, of the limitations and imperfections of this mathematical treatment, let us regard it merely as a temporary bridge leading towards a wider point of view.

Taking decimally increasing values for d, we get

d	d^2	d^3	$\frac{1}{d^2}$	$\frac{1}{d^3}$
0.01	0.0001	0.000001	10,000	1,000,000
0.1	0.01	0.001	100	1,000
1.	1.	1.	1.	1.
10	100	1,000	0.01	0.001
100	10,000	1,000,000	0.0001	0.000001

These values are not convenient to graph, and in order to show graphically the *relative* variation of the curves expressing specific surface and mean kinetic motion plotted against particle size, we may make use of figures covering a more limited range as follows:

d	d^2	d^3	$\frac{1}{d^2}$	$\frac{1}{d^3}$	$\frac{400}{d^2}$	$\frac{1000}{d^3}$
1	1	1	1.000	1.000	400	1,000
2	4	8	0.250	0.125	100	125
3	9	27	0.111	0.037	44	37
4	16	64	0.063	0.0156	25	15.6
5	25	125	0.040	0.0080	16	8
6	36	216	0.028	0.0046	11.2	4.6
7	49	343	0.020	0.0030	8	3

The values of $\frac{1}{d^2}$ and $\frac{1}{d^3}$ have been multiplied by different constants to make their curves, when they are plotted as ordinates against the values of d as abscissas, occupy about the same relative positions as we find when we compare the kinetic motion of particles in hydrosols having a diameter of about 1 μ with the specific surface of such particles.

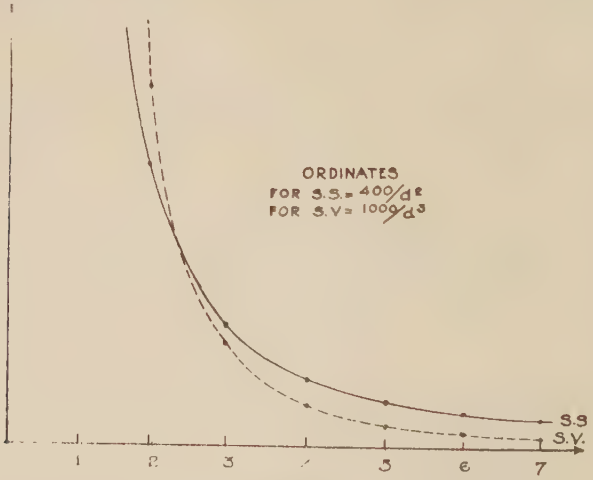

FIG 2.

Graphing the values of $\frac{400}{d^2}$ and $\frac{1000}{d^3}$ as ordinates against the values of d as abscissas, we get the curves shown in Fig. 2, *S.S.* being the specific surface curve and *S.V.* the volume curve. Their relation is obviously of the same nature as the diagrammatic curves in Fig. 1 showing specific surface and kinetic motion plotted in accordance with experiment and observation. This is only to be expected, since mass is generally proportional to volume, and kinetic motion varies as the mass (the formula for momentum being MV where M is the mass and V the velocity).

The balance between specific surface and kinetic motion is also important in controlling the formation and growth of nuclei, which occur in all cases of the solidification of fluid melts, and of precipitate and gel formation. Thus T. Svedberg[5] states: "The spontaneous formation of nuclei in a molten substance might be connected with the distribution curves of the velocities of the molecules (Fig. 3). Probably there would be a certain range of velocities that favors the production of nuclei. If the velocity is too high, the molecules will not stick together to form an aggregate; if too slow, the chance of meeting will be very small. If we lower the temperature, the distribution curve will move in the direction indicated in the figure and the velocity of production will increase; when it has passed the maximum it will decrease again."

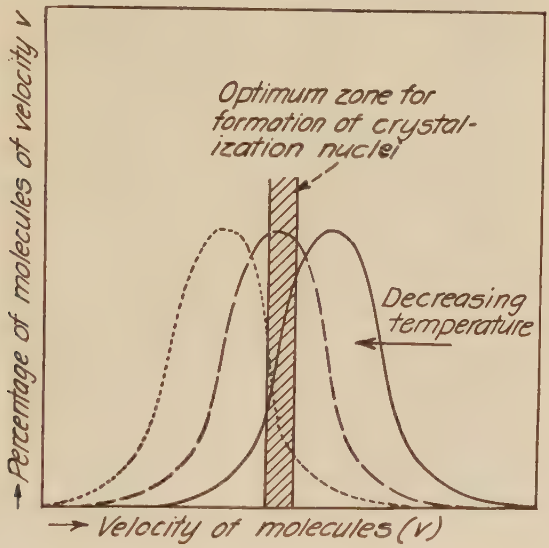
Optimum zone for formation of crystalization nuclei
Decreasing temperature
→ Percentage of molecules of velocity v
→ Velocity of molecules (v)

Fig. 3.

From what has been said it is evident that the zone of maximum colloidality must be a basic phenomenon, and we should therefore expect to find very widely scattered evidence of it. A few instances of its occurrence will be mentioned to show that this is so.

Wolfgang Ostwald[6] has pointed out the sharp viscosity maxima observed in the heat coagulation of *egg albumin* and in the formation of *starch pastes.* In fact when a suspension of starch granules is heated, the viscosity rapidly rises to a maximum and steadily falls off as dispersion, accompanied by chemical changes, continues. The same phenomenon is observed in starch pastes made cold, with alkali.

R. Auerbach[7] points out that coarsely dispersed *dyes* like Benzopurpurin 4B and Azo-blue dye better when more finely dispersed by heat, whereas finely dispersed dyes like Heliotrope 2B and Erika BN dye more poorly under these conditions. Evidently then one of the factors in the "driving on" action of acids and salts (Glaubers salt, NaCl) used as adjuncts to certain dye baths, is the aggregation of the dye particles to an optimum degree of dispersion. F. Sproxton[8] found that when water is gradually added to acetone dispersions of *nitrocellulose,* the viscosity of the dispersion goes through a maximum, both absolutely and relatively to the solvent. Quite a similar case is mentioned by C. G. Storm (to appear in Volume III of this series). A 4 per cent solution of nitrocellulose (12.2 per cent N) gave the following results with a falling sphere viscosimeter:

	Ether Per Cent Vol.	Alcohol Per Cent Vol.	Viscosity t
Slightly jellied	80	20	160.7
	75	25	59.6
	70	30	39.9
	60	40	28.8
	50	50	23.1
	45	55	26.1
	40	60	30.5
Slightly jellied	30	70	90.4

Storm found that with 3 to 6 per cent solutions of nitrocellulose, the minimum viscosity was given with 55 per cent ether and 45 per cent alcohol. The lowest viscosity corresponds with greatest solubility or dispersion.

In the case of a mixture of butyric acid and water, containing 38.6 per cent acid, Wo. Ostwald (*loc. cit.*) observed a sharp maximum in viscosity which changed as much as 34.3 per cent per degree.

The viscosity of *sulphur* rises enormously in the neighborhood of 200° C. and falls abruptly again. At 150° it is 8, at 200° it is 50,000, and at 400° it is 150. Wo. Ostwald (*loc. cit.* and Grundriss, 2nd ed., 1911, p. 128) comments on the relation between this behavior of sulphur and that of critical fluid mixtures.

In the case of metals we have several instances of the zone of maximum colloidality. Thus Merica, Waltenberg and Scott[9] point out that *duralumin* undergoes spontaneous annealing, the hardness reaching a maximum and then falling off. With *steel* we see a similar optimum hardness in hardenite; the coarser Martensite, Troostite, Sorbite and pearlite being progressively softer, whereas the finer Austenite is likewise softer.[10]

A. Sauveur in the 1st Howe Lecture (1924) before the American Institute of Mining and Metallurgical Engineers points out that on heating pure iron (Armco iron), after a preliminary softening the metal begins to harden again at a little over 900°, reaches a maximum at about 980°, and softens again as fusion is approached.[11] This hardening leads to red-shortness between 900° and 1025°, the lack of plasticity being a maximum between 930° and 1000° C. (See Fig. 4.) It is interesting to note that manganese, which acts as a "protector" or inhibitor of aggregation even in the presence of sulphur, tends to prevent red-shortness in steels.[12]

It is well known that hammering or severe cold working metals generally makes the grain finer and hardens the metal. Rawdon and Mutchler found that on continued cold rolling that softening again occurred. Evidently they crossed the optimum zone.

Wo. Ostwald[13] points out many alloys reach their optimum technical properties at a *mean,* that is, colloidal degree of dispersion, and not at the highest or molecular dispersion.

Slightly hydrolyzed gelatin makes a stronger joint than the original high test gelatin, or than when highly hydrolyzed,[14] and glue is stickiest when between the fluid and gel state.

A striking instance of the zone of maximum colloidality is given in the experimental results of McBain with soap (see this volume, p. 137). The first traces of salt added to a solution of, *e.g.*, sodium palmitate lower the viscosity, more salt increases it, and with still more salt the viscosity reaches a maximum and drops before the limits of homogeneous dispersion are reached. Finally, excessive amounts of salt liquefy the jelly. Martin H. Fischer ("Soaps and Proteins") showed with sodium salts of the fatty acids, the water holding capacity increases as we pass up the series; the caproate shows signs of holding water, while 1 mol of Na caprylate gives a jelly with 250 c.c. of water. L. Lascary[15] reports that the effect of sodium soaps on surface tension *increases* with molecular weight to sodium myristate, above which it *decreases.*

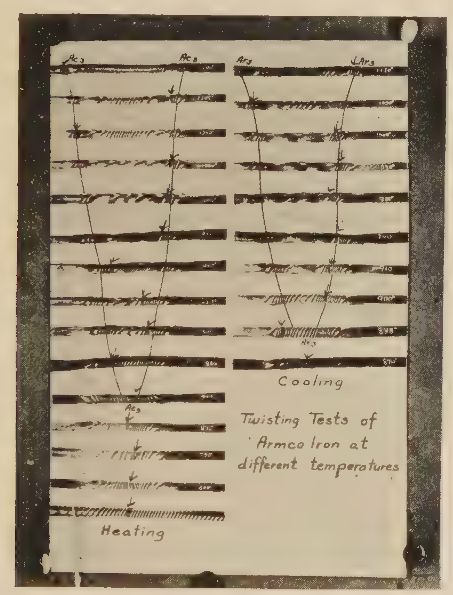

FIG. 4.

Viscose shows a maximum viscosity during ripening. The *comet's tail* consists mainly of particles of the intermediate colloidal size which are repelled by the solar "light pressure."[16] *Clouds* consist of water droplets too small to fall rapidly, and too large to act as vapor or gas. Escaping steam becomes visible as it approaches the colloidal zone, and fades away as the growing droplets pass out of it.

A most striking example of optimum dispersion is found in living matter. Figuratively speaking, if all the chemical substances comprising our organism were in true or crystalloid dispersion, reactions would proceed so rapidly that we would, so to say, live ten years in ten minutes. On the other hand, if coarse dispersion prevailed, it would take ten years to live ten minutes. Every organism is dependent upon the coördination of its chemical reactions *in point of time,* and this leisurely procedure depends largely on *degree of dispersion,* which keeps chemical reaction velocities within certain speed limits through its regulation of free surface and kinetic activity. Life lies between lysis and coagulation. The colloidal zone is, as it were, a vital metronome tolling off the tempo of life.

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11. See *Trans. Am. Inst. M. and M. Eng.,* 1925; *Mining and Metallurgy,* Oct., 1924; *Kolloid. Z.,* 36, 334 (1925).
12. See *e.g.,* J. Alexander, *J. Soc. Chem. Ind.,* 1909.
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15. *Kolloid. Z.,* 34, 73 (1924).
16. J. Alexander, "Colloid Chemistry"; *J. Popular Astronomy,* 1925.

The following seem to be instances of the zone of maximum colloidality:

Iron reduced by hydrogen for one hour, shows maximum pyrophoric action if reduced at 600° (A. Smits and G. Wallagh, *Rec. trav. chim.,* **44**, 130 (1925)).

Mixtures of sodium stearate and oleate have a viscosity 6-40 times that of either alone; the mixture shows ultramicroscopic threads (Freundlich and Kores, *Kolloid Zeit.,* **36**, 241 (1925)).

The toxicity of fatty acids to insects increases to about C_{10} (capric acid) and then falls (E. H. Siegler and C. H. Popenol, *J. Agri. Rev.,* **29**, 259 (1924)).

Sodium thiocyanate produces a maximum viscosity in gelatin solutions at about 1N. Change in particle size may be due to change in aggregation or in hydration (E. Stiasny, *Kolloid Zeit.,* **35**, 353 (1924)). Optima occur in the swelling of gelatin in aqueous solutions of formaldehyde, glycerol, phthalic acid, Mg and Mn salts (Popoff and Seisoff, *Biochem. Z.,* **156**, 97 (1925)).

Optimum yeast growth occur at concentrations of ammonium salts which give minimum swelling of wheat glutin (E. I. Fulmer, 2nd *Colloid Symposium Monograph,* 1925, p. 204).

Encolloidality in organisms. (See H. Schade, Vol. II; L. Seitz, *Gynäkol,* **124**, 25 (1925).)

Theory of the Colloid State of Matter*

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I. Brief Historical Introduction

It is not quite correct to say that *Thomas Graham* was *quite positive* in denying to colloids the ability to crystallize, and to crystalloids the ability to display colloidal properties.

As will be realized from *Thomas Graham's* own words quoted below, he actually conceded both: *e.g.,* the display of colloidal properties by as typical a crystalloid as ice, and the crystallizing ability of as typical a colloid as albumen.

> "Ice itself presents colloidal characters at or near its melting point, paradoxical though the statement may appear. When ice is formed at temperatures a few degrees under 0° C., it has a well marked crystalline structure, as is seen in water frozen from a state of vapor in the form of flakes of snow and hoar-frost, or in water frozen from dilute sulphuric acid as observed by Mr. Faraday. But ice formed in contact with water at 0° C. is a plain homogeneous mass with a vitreous fracture, exhibiting no facets or angles. This must appear singular when it is considered how favorable to crystallization are the circumstances in which a sheet of ice is slowly produced in the freezing of a lake or river. The continued extrication of latent heat by ice as it is cooled a few degrees below 0° C., observed by M. Persons, appears also to indicate a molecular change subsequent to the first freezing. Further, ice, although exhibiting none of the viscous softness of pitch has the elasticity and tendency to rend seen in colloids. In the properties last mentioned it suggests a distant analogy to gum incompletely dried, to glue or any other firm jelly.
>
> Ice further appears to be of the class of adhesive colloids. The reintegration (regelation of Faraday) of masses of melting ice when placed in contact has much of a colloidal character. A colloidal view of the plasticity of ice demonstrated in the glacial movement will readily develop itself.
>
> A similar extreme departure from the normal appears to be presented by a colloid holding so high a place in its class as albumen. In the so-called blood-crystals of Funke, a soft and gelatinous albumenoid body is seen to assume a crystalline contour. Can any facts more strikingly illustrate the maxim that in nature there are no abrupt transitions, and that distinctions of class are never absolute?"

Thomas Graham was, however, not quite clear as to the conditions to be fulfilled in order that the transition should take place from the colloid to the crystalloid state and vice versa.

Thomas Graham himself admits that these conditions "remain still a mystery", though he indulges in a few correct speculations concerning the conditions under which the crystallizing tendency of the colloids would assert itself.

> "Dilution," says Thomas Graham, "no doubt weakens the colloidal character of substances, and may therefore allow their crystallizing tendency to gain ground and develop itself, particularly where the crystal once formed is completely insoluble as with quartz."

While the above quoted and other ideas of *Thomas Graham* of similar purport received no attention in the scientific world, his assertions, viz.:—

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* Translated from Russian by S. F. Slokasoff, Chem. Eng.

that the colloid substances would be "marked out by the absence of power to crystallize," that the colloids and the crystalloids would be "like different worlds of matter," that the dissimilarities between these two worlds would be as sharp as those "between the material of mineral and the material of an organized mass"—these and similar assertions were constantly repeated by everybody, and were introduced into most of the text-books on chemistry and physics, to appear in the chapters dealing with the colloids.

I have no knowledge that, up to 1906, any of the investigators of colloids had ever set himself the task, to disclose—by way of a *systematic experimental* investigation of the *process of crystallization of different substances from solution*—the transition conditions from Colloid to Crystalloid and vice versa, which conditions remained a "mystery" to *Thomas Graham.*

Nor is it known to me that, up to 1906, any scientist had ever given—in one way or in another—an experimental, or even a theoretical basis to the *law* of the universality of the colloid state.

As regards not the law itself of the universality of the colloid state, but merely isolated ideas and surmises, implying an interpretation of the colloid state as either a state proper—however only qualitatively—to substances belonging to *all* classes of our chemical system, or as some *unstable* condition, which must apparently be gone through by *all* substances when precipitating from solutions (*e.g.,* especially in the cases of so-called amorphous precipitation, if interpreted as a segregation process of liquids), and the like—such ideas and surmises have actually been voiced even before 1906 by some scientists.

In the above sense,* statements were made by *J. M. van Bemmelen* (1898), by *D. I. Mendeléef* (1902), and by *A. Mueller* (1903).

But of all these ideas, of all these surmises not a single one did ever imply —or even vaguely hint at—the possibility of the existence of *notably* a colloid state that, under conditions properly selected would for *any* substance whatever be as *quantitatively stable in time* (e.g., *extremely* stable), as it happens to be with some given substance or other.

And therefore one may aver that, at the moment when I was publishing my investigations, *the idea of the universality of notably such a colloid state* as, subject to properly selected conditions, is for the whole number of substances, *equally quantitatively stable in time* † (e.g., *extremely* stable), *was an entirely new idea.*

My investigations which led me to the theory of the colloid state—which will be explained in the later chapters of the present paper—were carried out in 1905 and 1906.

In the latter half of 1905 I began my systematic experimental investigations on the influence exerted by the concentration of the reacting solutions on the process of precipitation of *solid* substances but slightly soluble in water, and of *solid* substances which, while being *readily* soluble in water, are but slightly soluble in solvents other than water (*e.g.,* $CuCl_2$ in benzene).

During the initial period of my investigations, I did not yet introduce any alterations of my own into either the concept "amorphous precipitate" or the concept "colloid state."

Nor did I initially treat those factors separately from each other, which suffer quantitative changes whenever the concentration of the reacting solutions changes; I contented myself with classing these factors together as "Internal Resistance to Crystallization from Solutions" or simply as "Resistance in Solution."

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* It should be noted, however, that, at the time when they were uttered, such ideas failed to exert any influence on the development of the teaching of the colloids, and that I was actually the first to mention them in my publications.

† See below: Tables II and III; aluminium hydroxide and barium sulphate respectively.

It is but natural, of course, if the crystallizing ability of a substance, *under certain well-defined conditions,* is said to be greater, the larger are the crystals which, *under the same conditions,* would separate out from a solution of this substance.

Hence it is reasonable to designate as "Internal Resistance to Crystallization from Solution," the *totality* of the conditions prevailing during the precipitation of substances from their solutions, by which the substance is coerced to separate out, now in large, and now in exceedingly small crystals, now under the shape of an amorphous precipitate, and now as a colloid formation.

Before January, 1906, my study of the influence of the concentration of the reacting solutions on the precipitation process was already completed for 63 different substances selected in an *arbitrary* manner.

Since, however, these substances were taken *at random;* since in all cases, the influence of the concentration on the precipitation process proved, in a general way, to be the same; and since, finally, I was able to convert into the colloid and the amorphous states every substance of these 63 substances, I felt myself entitled—in my communication, "The Colloid State as a Universal Property of Matter," delivered before the Russian Chemical Society on February 15 (2), 1906, to establish the following principles:

> I. "By increasing the resistance to the forces tending to bring the particles into an arrangement characteristic of a crystal, we shall obtain any substance in the colloid state; conversely: on weakening this resistance, any substance will separate out in the crystalline state."
>
> II. "The colloid, the amorphous and the crystalline states are just as universal with matter, as the property of matter is universal, to appear in the three states of aggregation; just as the realization of these latter states for all substances has ever required, and still requires, an expenditure of time and effort, and also the application to the substance of more and more powerful agents, so is the preparation of all solid substances in the colloid, the amorphous and the crystalline states dependent on the same factors."

From other deductions, one more shall here be quoted:

> "For a given substance, no sharp boundary lines may be drawn between the colloid, the amorphous and the crystalline states, since the mutual transition from one state to another is affected by degrees, as the resistance is overcome to the forces which tend to bring about separation of the substance in the crystalline state."

It will clearly be realized from the above literal quotations, that my deductions were merely a generalization of my experimental results obtained with the above 63 *arbitrarily* selected substances.

These deductions were nothing of a *conjecture,* nor were they a *theoretical speculation;* as a matter of fact, *not alone was the idea on the universality of the colloid state* embodied in these deductions, but they *represented the law itself of the universality of the colloid state, established on experimental grounds.*

In the course of my further experimental work during the same year 1906, I convinced myself that the particles of the amorphous and the colloid systems were, no doubt, crystalline; and that therefore, the amorphous and the colloid states could not be treated as two separate states of matter, seeing that both the amorphous and the colloid systems contained the substance in a *solid, crystalline* state, but only while in extreme subdivision.

On the 20th (7) of December, 1906, I communicated these results to the

Russian Chemical Society, in my paper: "Some Contributions to the Question as to Whether or Not the Colloid and the Amorphous are Independent States."

In this same communication, and once again in my communication delivered before the Russian Chemical Society on April 18 (5), 1907, I pointed out that the principles and the laws I had been able to deduce, which regulate the size of the particles of *solid* phases separating *from liquid solutions,* ought to be generalized so as to cover *all* cases of *new* phases coming into existence.

Finally, in my communications read before the Russian Chemical Society during 1907, I was able to show *firstly:* that the colloid state must *always* be passed through, whenever already existing phases *disappear* (*e.g.,* when substances dissolve, evaporate, and the like), and *secondly:* that particles (molecules and molecular complexes) similar in size to those present in colloid systems may, under some well-defined conditions, also exist in such systems as, according to the Phase Rule, are classed with the one-phase systems.

During the same years 1906 and 1907, I also succeeded in deriving the law of the universality of the colloid state—in its above broad interpretation—by way of *deduction;* namely, from a theoretical analysis of both the processes of formation of new phases, and the processes of already existing phases passing away, and the like.

And so, in the years 1906-1907, I have been able to establish, both inductively and deductively, the law of the universality of the colloid state,—not of a state that would be quantitatively different with the various substances, but of *a state that, whenever realized under properly selected conditions, is quantitatively the same for all these substances;* and besides, I have succeeded in giving to the concept of the colloid state so wide an extension as, up to that time, it had never received.

In this place it should be mentioned that, among contemporary investigators of the colloids, I know but one who, in his endeavors to work out a rational classification of the colloids, went the same length as I did—and this quite independently of my above investigations—in extending the concept of the colloid state, so as to comprise all cases of the coexistence of different phases, not merely those of the systems consisting of liquids with solid particles suspended therein.

This investigator was the German scientist *Wolfgang Ostwald,* who, in April-May, 1907, published his work: "Contributions to the Systematics of Colloids," which since became classic, and which contains a rational classification of disperse systems.

From this very brief historical introduction it may thus clearly be seen that my theory of the colloid state, of which the fundamental principles will be explained in later chapters of the present paper, has arisen as the result of my experimental work in studying the processes of precipitation of solid substances, accomplished in the latter half of the year 1905; in my works of 1906 and 1907, this theory has received a further and wider development, on both experimental and theoretical lines.

To be as brief as possible, my theory of the colloid state will be presented in this paper for the cases *only,* of solutions of *solids* in *liquids,* and for the cases of the appearance and disappearance of *solid* phases in *liquid* media.

I wish, however, to emphasize at the outset and most emphatically that, as was already pointed out in my publications dating as far back as the years 1906 and 1907, the principles and the laws deduced by myself for the cases mentioned above, are equally valid—with but inconsiderable additions and modifications—for the cases of *other* solutions (*e.g.*, for solutions of liquids in liquids, and so on), and for the cases of the appearance and disappearance of *other* phases, and not of solid phases alone.

After having made this remark, which I consider to be very essential, I shall now proceed to the presentation of the fundamental principles of my theory of the colloid state.

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author began to appear regularly in *Koll. Zeit.* (respectively in *Kolloidchem. Beih.*), where they may easily be found.

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II. The Fundamental Principles of the Theory

1. All the properties (both chemical and physical *), which earlier were considered as specific for colloid substances, appear spontaneously with *every* solid substance as its subdivision progressively increases, irrespective of the means by which this subdivision is brought about (*e.g.,* whether they be chemical, physico-chemical, physical, mechanical, and the like).
2. Any solid substance, regardless of what its chemical nature or any of its other properties may be, must always pass, on dissolving, through a *colloid stage of solution.*

And in fact, if, with a size of the crystalline grains falling below the limits of microscopic resolvability, the colloid properties (Principle I) begin to assert themselves sharply, it is obvious that, were we to stir up a pinch of some powdered substance in a liquid in which it is able to dissolve, the grains of this powder must necessarily pass through a *colloid stage of solution,* previous to their complete dissolution, *i.e.,* before they break up into molecules (in special cases—into atoms).

For the cases of solid substances *rapidly* dissolving in the liquids selected, the time intervals, during which this *colloid stage* of solution would persist, will naturally be very small, but nevertheless, even for these cases, the existence of a *colloid stage of solution* is beyond any doubt.

3. Any solid substance, regardless of what its chemical nature or any of its other properties may be, must always pass, on crystallizing, through a *colloid stage of crystallization.*

For the cases of a *rapid* increase in size, *i.e.,* of rapid growth of the vanishingly small crystals initially formed, the time intervals, during which the *colloid stage* of crystallization would persist, will naturally be very small, but nevertheless, even for these cases, the existence of a *colloid stage of crystallization* is beyond any doubt.

The Principles 2 and 3 indicate that the colloid stages of solution and crystallization will take place for *any* substance and under *any* conditions whatsoever of solution and crystallization; but the intervals of the existence of these *colloid* stages may not always be of a duration that would suit some purpose or other of ours. My theory of the colloid state maintains that:

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* My theory of the colloid state is neither *purely-chemical,* nor is it *purely physical;* it is a *physico-chemical* theory, inasmuch as it takes into account both the physical and the chemical factors. This has duly been pointed out for the first time (so far as I know) by the Italian scientist *Leonardo Cassuto,* when classifying the various theories of the colloid state in his work: "Lo stato colloidale della materia," Pisa, 1911, pp. 258-268. German Translation: "Der kolloide Zustand der Materie," S. 226 (1913). Verlag von *Th. Steinkopff,* Dresden.

4. For *any* substance, such physico-chemical conditions of crystallization and solution may, according to one's wish, be realized at which the colloid stages of crystallization and solution would last for periods of time, of which the corresponding durations may be varied, according to the above mentioned conditions, within extremely wide limits, viz.: from such practically vanishingly small values as amounting, *e.g.*, to fractions of a second and seconds, up to such large values as measured by years, decades and even centuries.
5. For *any* given solid substance, suitable solvents and such temperature conditions may be found, at which, in the solutions of this solid substance in the above solvents, large molecular complexes will form by way of solvation and association, subsequently to persist in a state of kinetic equilibrium, which (*i.e.*, complexes) will not be inferior in size to the particles existing during the colloid stages of solution and crystallization of substances (*vide:* Principles 2, 3 and 4).

To the same species of the colloid state also belong solutions of such solid substances, whose molecules contain *a large number of atoms condensed by ordinary chemical forces* (*e.g.*, the proteins and the like), or—to put it in another way—the solutions of substances of composite chemical nature.

Having thus briefly stated the fundamental or the general principles of my theory of the colloid state, I shall next proceed to a brief special consideration of the conditions under which *stable* colloid formations will arise; but, before anything else, the fundamental laws governing the precipitation of solid substances from their solutions in liquids must here be treated.

III. The Fundamental Laws Governing Precipitation of Solid Substances from Their Solutions in Liquids

The fundamental laws which will be treated in the present chapter were established by me in 1906 as deductions directly derived from a comprehensive volume of experimental results.

For the easy understanding of these laws, above all, the conditions must be clearly defined, under which the processes of precipitation of solid substances from solutions were studied.

This will be done in the first instance.

In the second instance, in order to facilitate the apprehension of the laws of precipitation subject to our consideration, I shall first treat them for the most simple of theoretically *idealized* cases, and subsequently proceed to the *real* cases.

A. The Conditions which were Fulfilled while Studying the Precipitation Processes of Solid Substances from their Solutions in Liquids.

The crystallization of a substance from its solutions may either be *"spontaneous,"* or it may be *"produced by the introduction of germs"* of the crystalline substance into supersaturated solutions of the substance.

It is precisely *spontaneous* crystallization, to which the laws to be explained below apply.

This is the first condition.

The second condition concerns the volumes of the solutions applied for crystallization purposes.

It is an elementary truth that it is impossible to obtain from a microscopic droplet of a solution (*e.g.*, of NaCl in water) crystals as large as those which may be obtained from one litre of the same solution.

No less is it obvious that, for obtaining NaCl crystals of the same magnitude (*e.g.*, crystals weighing 1 gram) from a solvent in which the solubility of NaCl is equal to 20 grams per 100 c.c. solvent, and from some other solvent, in which the solubility of NaCl is but 0.0002 of a gram, different volumes of the solutions are to be applied, be it for no other reason than that no such quantity as 20 grams, but only two ten-thousandth parts of a gram of NaCl, is present in 100 c.c. of the solution in the latter case.

The condition concerning the volumes of the solutions applied for crystallization is equally important from the practical, as well as from the theoretical standpoint.

In the theoretical analysis of the precipitation processes, in order to exclude *completely* the influence of the volumes on the results of the crystallization processes, crystallization is assumed (this is, of course, a *purely theoretical* assumption) to take place, out of *unlimitedly large* volumes of the solutions.

The bearing of this assumption (which *cannot be fulfilled in reality*) on the theory of the crystallization processes will become quite clear in the course of further discussion.

The condition which serves, in real cases of precipitation, to exclude *practically* the influence of the volumes * consists in applying for crystallization purposes such volumes of the solutions as would warrant,—for all cases, *subject to comparison,* of precipitation,—the same amount, *in gram-molecules,* of precipitates *at the end of the crystallization process.*

In order to fulfil such a condition, we should obviously take the slightly supersaturated solutions in correspondingly larger volumes than those taken of the strongly supersaturated ones.

It will readily be understood that it is only if this condition concerning volumes has been satisfied, that we may be absolutely certain that the small crystals, obtained at a given supersaturation, have been produced, not because of any shortage of substance, due to inadequately small volumes of the solution having been applied, but as a result of the factors regulating the crystallization process, quite independently of the above shortage.

Whenever crystallization occurs "instantaneously" (as perceived by our senses, of course,—not absolutely), the influence of the volumes is practically of no importance, or better let us say—it is vanishingly small.

And in point of fact, if we pour together a 7-normal aqueous $Ba(CNS)_2$ solution and a 7-normal $MnSO_4$ solution, the result of precipitation will be the same, whether we take 1 c.c. or 1000 c.c. of each solution, *provided that the velocity of pouring together and stirring the solutions was the same in both cases;* we shall obtain in both cases an equally extremely fine-crystalline precipitate of $BaSO_4$ (of so-called "amorphous-flocculent" appearance).

If, on the other hand, the concentration of the reacting solutions is *e.g.*, equal to or smaller than 1/5000 normal, the result obtained in crystallization of the same $BaSO_4$ (with regard to the crystal size) will largely depend on the volumes taken of the reacting solutions; with the above mentioned concentrations the crystallization process will no longer be "instantaneous."

In order that the above treated condition be kept in practice, the volumes taken of the reacting solutions must be correspondingly larger for small concentrations, than for the larger ones; and on comparing the results obtained in crystallization for substances having *different* solubilities, correspondingly larger volumes of the solutions are used for the less soluble substances.

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* Perhaps it would be better, were we to speak of the influence of a shortage of substance in the very slightly supersaturated solutions, when small volumes of them are taken, on the magnitude of the precipitate crystals separating therefrom.

The third condition of rational study of the spontaneous precipitation processes of solids from solutions implies the most perfect elimination, so far as this is possible, of any *artificial* influences on the course of the crystallization process, such as *e.g.*, the *artificial* application of the centrifugal force, some kinds of special rays, electric energy, and the like.

Any *artificial* mechanical stirring is also excluded, after the crystallization process has set in.

The solutions undergoing crystallization must, certainly, always be thoroughly mixed together *before* crystallization begins, so as to secure as complete a homogeneity of the mixture as possible; but stirring during the course of the crystallization process means only introducing a factor which, being superfluous, tends to render the phenomena somewhat more complicated.

In other words, the conditions quoted above may, in the last item, be reduced to the requirement that, *having eliminated the influence of a shortage of substance in solution, on the crystal size of the precipitate* (the condition concerning volumes), we should study the laws governing *spontaneous* crystallization in its *natural* course, *i.e.*, without the introduction of any *artificial* agents that would influence the process from outside.

B. The Fundamental Precipitation Laws for Theoretically Idealized Cases.

In our further discussions, the following abbreviations will be used:

G_m = *mean* size of the precipitate crystals as measured in *gram-molecules.*

D_m = the reciprocal value of G_m; we may call it the *"degree of disintegration"* * of precipitates.

$(Q - L)$ = the difference between the concentration Q of the solution, the concentration which existed before the crystallization process has set in, and L the *ordinary* solubility of the substance constituting the precipitate. Q and L are both expressed in gram-molecular terms. *In some cases,* the difference $(Q - L)$ may be called the *initial absolute supersaturation* of the solution.

By way of idealization of real cases of precipitation, I developed the two following assumptions, which proved extremely helpful in simplifying the theoretical (and graphical) treatment of the question:

1a. The precipitation curves with the coördinates: G_m and $(Q - L)$ represent—*after the termination of the crystallization process*—hyperbolic curves, which are expressed by the general equation:

$$G_m \cdot (Q - L)^n = \text{const.}, \qquad \text{(A)}$$

where n is an integer number greater than zero; the values of n and those of the constant are varying, according to the conditions of the precipitation of the substance.

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* It would also be possible to call D_m the *"degree of dispersity,"* a term, which, in due time, was introduced by Wo. Ostwald—however, only to designate the relation of the surface of particles to their volume.

For the *simplest* of the theoretically idealized cases, $n = 1$; the equation (A) will then go over into the equation of a *bilateral hyperbola.*

1b. The precipitation curves with the coördinates: D_m and $(Q - L)$, represent—*after the termination of the crystallization process*—parabolic curves, which fit, all of them, into the general equation:

$$D_m = a \,.\, (Q - L)^n, \tag{B}$$

where n is an integer number greater than zero, and a is a constant; the values of n and of a vary, according to the conditions of precipitation.

For the *simplest* of the theoretically idealized cases, $n = 1$; the equation (B) will then go over into the equation of a *straight line.*

2. *After the end of the crystallization process, the dimensions of the precipitate crystals are no longer subject to alteration in the course of time.*

In other words, what we assume for the theoretically idealized cases, is firstly: that the re-crystallization process is entirely absent, *i.e.,* that there is no growth, with time, of the larger crystals at the expense of smaller ones.

And secondly: that, by way of aggregation of crystals, if they are ever so small, we may only obtain aggregates * (balls, flakes) of crystals, but never a *homogeneous* crystal like those obtained by way of *direct* crystallization.

In order to make this paper as concise as possible, I shall here discuss and illustrate by graphs only the precipitation curves with the coördinates: G_m and $(Q - L)$.

It will certainly not be difficult to apply, in a suitable manner, the general conclusions which we shall have drawn, also to the curves with the coördinates: D_m and $(Q - L)$.

It is easy to understand that, if for the *simplest* of the idealized cases, the equation holds:

$$G_m \,.\, (Q - L) = \text{const.},$$

then, for the same *simplest* case—if we go over to linear dimensions—(*e.g.:* cube-edge $= 1$), we shall have:

$$1 \,.\, (Q - L)^{\frac{1}{3}} = k.$$

In carrying out the theoretical analysis of the crystallization process, we may certainly avail ourselves of a variety of methods.

The most expedient method is, in my opinion, the one described below; since the beginning of my scientific work, *i.e.,* for about 20 years, I have always used this method, and it always proved of the greatest assistance to me, even when analyzing the most complicated cases of precipitation of substances.

Namely, the crystallization process is most conveniently split into two stages.

The first stage would comprise the condensation of molecules to molecular complexes—very minute crystals invisible even with the ultra-microscope (or, as upper limit, only just perceptible under the most perfect illumination conditions).

As will readily be understood, it is not only possible, but even necessary that to that stage we should apply the laws of chemical kinetics of homogeneous systems.

The second stage would then consist in the growth *through diffusion* of the minute crystals which were formed during the first stage of crystallization.*

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* The individual crystals constituting these aggregates may either be coadjacent or grown together.

It is not difficult to understand that it is already the laws governing chemical kinetics of heterogeneous systems which may and which must be applied to this second stage.

We could certainly calculate, in absolute measure, the velocity of the crystallization process—like the velocity of any chemical process—for any given moment of the *first* stage, from an equation of the form:

$$\text{Velocity of the process} = \frac{\text{driving force}}{\text{resistance}},$$

if only we were able to determine, for any given moment, the values of "force" and of "resistance" (W. Nernst[1]).

Since we are now discussing theoretically *idealized* cases, we may assume that determinations of this kind are possible; and if so, the velocity W during the first stage of crystallization, will be expressed by the formula:

$$W = k \cdot \frac{\text{crystallization (or condensation) pressure}\dagger}{\text{crystallization (or condensation) resistance}} \tag{I}$$

As regards the value of the velocity of crystallization V which prevails during the second stage of crystallization, it is given, conformedly to the *Nernst-Noyes-Whitney*[2] theory, by the equation:

$$V = D/\delta \cdot O \cdot (C - L), \tag{II}$$

where: $D =$ diffusion coefficient,
$O =$ surface of the growing crystal or crystals,
$C =$ concentration of the solution surrounding the crystal or crystals,
$L =$ solubility of the substance of crystals,
$\delta =$ length of the diffusion path (thickness of the adhering layer).

Previous to my clearing the question as to the quantities which are to play the parts of "crystallization pressure" and "crystallization resistance" in the formula for W, I shall draw (Fig. 1) three precipitation curves with the coördinates: G_m and $(Q - L)$.

These curves may be regarded either as obtained by the precipitation of the same substance from three different solvents, or by precipitation of three different substances from the same solvent, or, finally, by precipitation of three different substances from three different solvents.

Fig. 1 will help us to deduce, in part, the fundamental precipitation laws for theoretically idealized cases.

To begin with, how are we to understand the hyperbolic interdependence between the magnitude G_m of the precipitate crystals and the magnitude of $(Q - L)$?

Is not the hyperbola a curve, both of whose branches would touch the coördinate axes (which, in the present case, are also the asymptotes) at an infinite distance only?

If we abstract from our real possibilities, the above hyperbolic interdependence is to be understood in the sense as follows:

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* To be scrupulously exact, it should be noted that, during the first moments of crystallization, the second and the first stages will, to a certain extent, superimpose themselves upon each other, owing to the thermal non-uniformity, which is unavoidable with all really existing systems. If, however, we treat separately the first and the second stages, this will by no means affect the correctness of our deductions.

† By suitably selecting the units: $k = 1$.

1. Only with infinitely small $(Q - L)$, an infinitely large crystal may be obtained (*of course, with infinitely small velocities*), for any substance, from an infinitely large volume of a solution of this substance.
2. Only with infinitely large $(Q - L)$, such systems may be obtained for any substance, as consist of molecules disorderly scattered in space, *i.e.*, "amorphous" systems—if the atoms and the molecules be assumed as amorphous "per se" (*I have never agreed to accept this assumption. Still less am I inclined to do it now*).

If now we revert from abstraction to reality, the first of the above conclusions is to be understood to indicate that, with sufficiently small $(Q - L)$, it is possible to prepare *extremely large* crystals for *any* solid substance whatever.

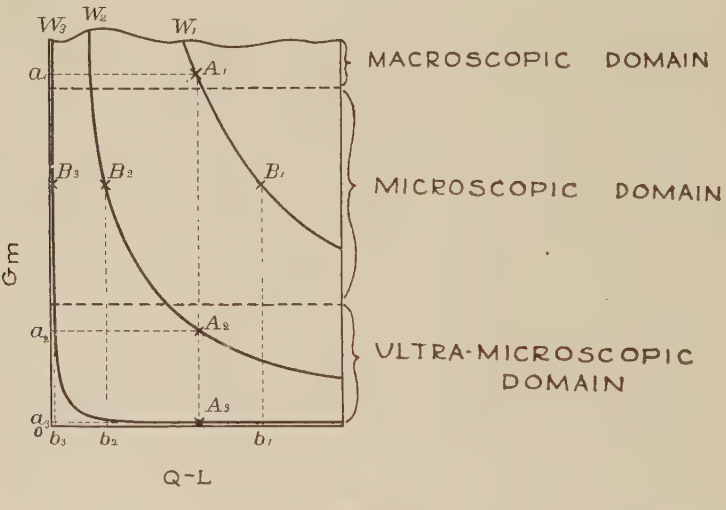

FIG. 1.

And our second conclusion—if we turn to reality—would imply that, with really attainable $(Q - L)$, and with really attainable mean* velocities, if these $(Q - L)$ and these velocities be ever so large, it is impossible to obtain absolutely "amorphous" solid systems; but if the $(Q - L)$ and the mean velocities are sufficiently large, it will be possible to realize, for every solid substance, such precipitates or, generally, such systems, as contain crystals of ultramicroscopic, and even superultramicroscopic dimensions.

It is not difficult to understand that this conclusion covers both the *law of the universality of the colloid state*, and the *principle of the impossibility of amorphous solid substances to exist in real Nature*.

What else do the precipitation curves with the coördinates: G_m and $(Q - L)$ in Fig. 1 tell us?

Among other things, they tell us that, for the same value of $(Q - L)$ and for the same substance, if it but crystallizes out from different solvents, the precipitates obtained after the completion of crystallization will greatly differ in average magnitude (G_m) of their crystals (see Fig. 1, points: A_1, A_2, A_3, which correspond to the same value of $/Q - L/$).

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* The mean velocity $= (Q - L)/t$, where t is the time elapsed from the beginning to the very end of the crystallization process.

Quite analogously, we may have—as a result of the crystallization process having completed itself—precipitates altogether identical with respect to the average magnitude of grain (G_m), but with very different $(Q - L)$, as will be clear, if attention is turned to the points: B_3, B_2, B_1, in Fig. 1, which all belong to the same straight line, running parallel to the horizontal coördinate axis, and which correspond to quite different values of $(Q - L)$.

Let us explain this by an example.

From nearly boiling H_2SO_4, it is the matter of but a few minutes, to obtain microcrystals of $BaSO_4$; let, for this case, $(Q - L) = ob_1$ (see point B_1).

Similar microcrystals of $BaSO_4$ can also be prepared from aqueous solutions; this, however, is only possible with $(Q - L) = ob_2$ which is many times smaller, and much more time will be needed than in the above case; accordingly, the mean velocity of crystallization will here be considerably smaller than it was in the above treated case (that of crystallization from boiling H_2SO_4).

And finally, by carrying out the formation reaction of $BaSO_4$ in mixtures of water and ethyl alcohol (*e.g.*, 50 per cent), we are also able, of course, to prepare microcrystals of $BaSO_4$ of the same average magnitude as in the two cases quoted above; here, however, the time necessary for the crystallization process to come to an end will be quite unusually protracted, because $(Q - L) = ob_3$ is extremely small; that is to say, the mean velocity will in this case be unwontedly small for ordinary laboratory work.

It should be stressed here that it is just owing to the lack of clearness concerning the relations just treated, that the teaching of the "amorphous" precipitates, of the "non-crystallizing" substances, was able to keep ground; a teaching which, from my point of view, deserves being classed down among the most absurd doctrines, which imply the most detrimental consequences.

Fig. 1 proves also helpful for obtaining a clear understanding of the very important law which, in due time, I called the *"Law of Corresponding States for the Crystallization Process."*

Let the precipitation curves in Fig. 1 be related, *e.g.*, to substances of different chemical composition.

Taking $(Q - L)' = ob_3$ as standard measure, the *corresponding* values of $(Q - L)$ for the two other substances—*i.e.*, values as would secure equal G_m—will be: (see point B_2 in Fig. 1) $ob_2 = j_2 \cdot ob_3 = j_2(Q - L)'$, and (see point B_1 in Fig. 1) $ob_1 = j_1 \cdot ob_3 = j_1(Q - L)'$; and so on, if the number of curves drawn in Fig. 1 be greater than three.

The quantities: $(Q - L)'$, $j_1(Q - L)'$, $j_2(Q - L)'$, . . . are the *corresponding* quantities (there will, of course, be *corresponding* mean crystallization velocities correlated to them), with which the substances: X_0, X_1, X_2, . . . X_n, of different chemical composition, would yield, after complete termination of the crystallization process, precipitates of the same mean magnitude of crystal-grains (G_m).

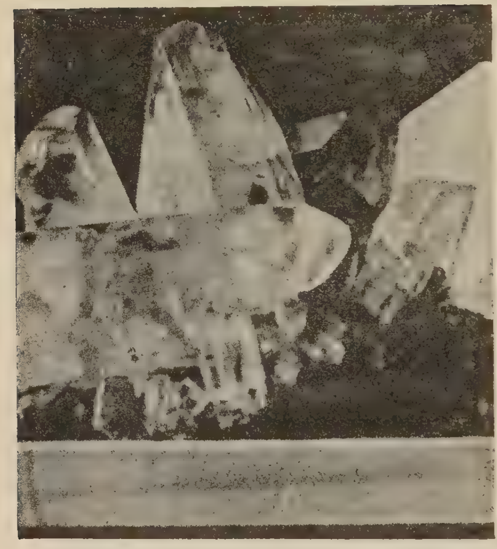
In other words, *with corresponding values of* $j \cdot (Q - L)$, *all substances, whatever their chemical composition, will appear, after the end of the crystallization process, as precipitates, of which the mean magnitude of crystals* (G_m) *is the same.*

And this is the *"Law of Corresponding States for the Crystallization Process"* in its *quantitative* formulation; this formulation cares little for either

PLATE Ia.

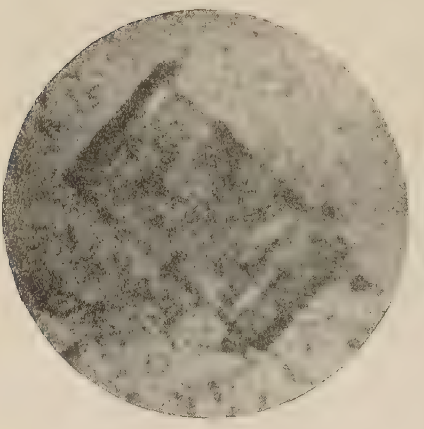
Precipitates of $BaSO_4$.

Precipitates of NaCl.

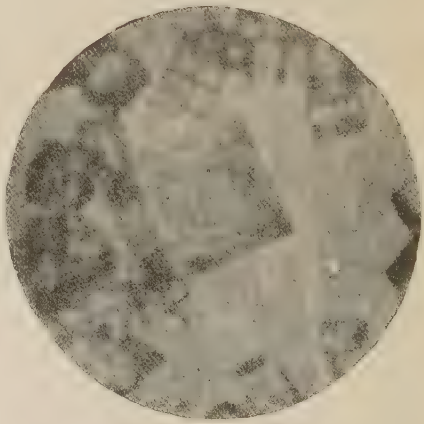


No. 1.
About 0.65 of the natural size.

No. 5.
About 0.6 of the natural size.

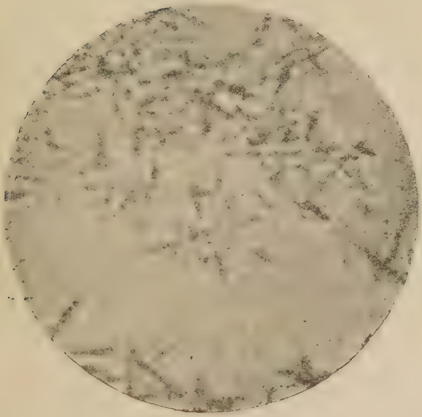


No. 2.
Magnification: about 850.

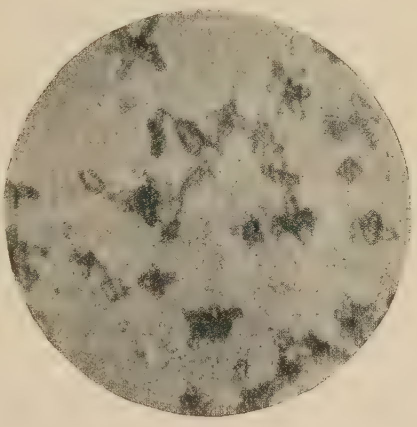


No. 6.
Magnification: about 400.

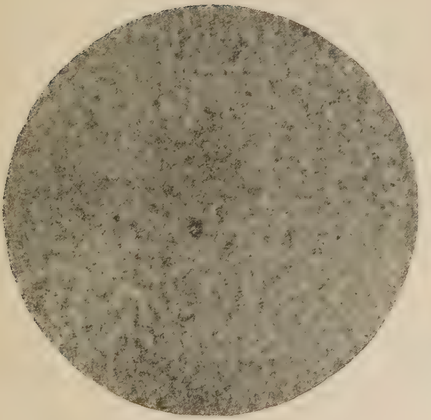
Plate Ib.



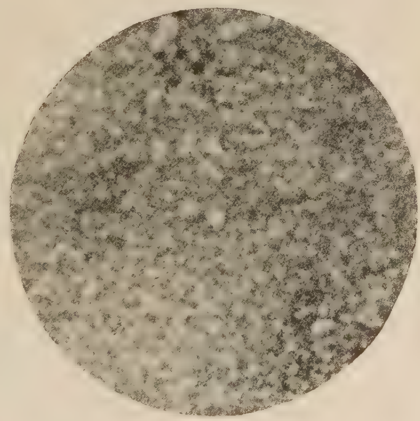
No. 3.
Magnification: about 2000.



No. 7.
Magnification: about 400.



No. 4.
Magnification: about 2000.
Colloid precipitate.



No. 8.
Magnification: about 2300.
Colloid precipitate.

the form of the contours of the crystals, being merely concerned with the mean magnitude G_m of these crystals.

Dependent on the values of the quantity $(Q - L)$, the substances may also separate out in a variety of "qualitatively" different precipitate patterns.

The grains of the precipitates may, for instance, represent holohedral crystals (see Plate I; microphotographs No. 1, 2, 5, 6), or figures of growth (No. 3, 7), or finally, they may display a very fine-grained structure and be of flaky-gelatinous consistency (No. 4, 8), and so on.

The microphotographs in Plate I are pictures of NaCl and $BaSO_4$ precipitates.[3]

Suppose, for instance, that the formation of figures of growth is taking place, for some particular substance, with a certain value $(Q - L)_a$, while the same occurs, for other substances, with the values: $j' . (Q - L)_a$, $j'' . (Q - L)_a$, . . . and so on, respectively; these values of $(Q - L)$ will then fulfil the rôle of *corresponding* values for the whole number of substances concerned in the *given* set of experiments.

Similar *corresponding* values of $(Q - L)$ can also be established for other "qualitatively" different precipitate forms; and if so, we may assert that:

With corresponding values of $(Q - L)$, any substances whatever can be prepared in whatever "qualitatively" identical precipitate form may be desired.

This is another formulation of the *"Law of Corresponding States for the Crystallization Process,"* so to say, from its *"qualitative"* side.

The possibility of preparing "qualitatively" identical forms of precipitates must certainly not be interpreted in the sense, *e.g.*, of the possibility of obtaining, for a substance which habitually crystallizes in some definite kind of symmetry, figures of growth as would correspond to whatever other kind of symmetry; this is impossible: and it is therefore that the figures of growth for the NaCl (see microphotograph No. 7) are built up in a different manner than are those for the $BaSO_4$ (see microphotograph No. 3).

And further, the figures of growth of the so-called *strongly negative* crystals will be shaped as long, fine needles, and the corresponding precipitates will display a "fibrous" or "filiform" structure (similar "fibrous" or "filiform" precipitates, *i.e.*, precipitates consisting of fine, long microneedles, are yielded, *e.g.*, by: asbestos, soaps, acid barium sulphate, $CaSO_4 . 2H_2O$, $SrSO_4 . 2H_2O$, silver acetate, and a large number of other substances).

The *strongly positive* crystals,—in which the points of the network are most densely massed in a *singular plane*, in which lie the directions of maximum cohesion and most intense growth,—being characterized by a *tabular* habit, can assuredly not be expected to change "qualitatively," under the influence of a change in the *mean* velocity of crystallization, the form of their crystalline precipitate grains in *exactly the same* manner as do the *strongly negative* crystals, these latter being possessed of a *singular direction* of maximum cohesion, which is also the direction of most intense growth; this accounts for the *prismatic* habit of such crystals.[4]

In other words, on changing the values of $(Q - L)$—and consequently also the mean velocities of crystallization corresponding to these values—we may produce, for any substance, any alteration desired in the *magnitude* of the precipitate grains (crystals); we may also obtain, for any substance, precipitate forms such as curdy, flaky, and the like; but with regard to the changes in the contours and the internal structure of the grains, the influence of the value of the magnitude $(Q - L)$ is confined to the kind of symmetry characteristic of the substance, and to whether its crystalline complexes are *positive* or *negative* ones.

In order to make ourselves a clear idea as to the compass and the contents of the *"Law of Corresponding States for the Crystallization Process,"* the understanding is very essential, of the true meaning of the restriction we just introduced into the "qualitative" formulation of the above law, by taking into account the crystallographic structure of the substances undergoing precipitation.

By bringing the solution to crystallize out when in very thin layers, *e.g.*, when pressed between two plane glass-slides, we may obtain "flat" crystals, "flat" figures of growth, and so on, for every substance.

In the above, and in similar cases, just as in all preceding cases of crystallization, with corresponding values of $(Q - L)$ we obtain identical results.

It also deserves being mentioned here that, for the *existence* of the *"Law of Corresponding States for the Crystallization Process,"* it is immaterial, whether the precipitation curves are exactly such hyperbolic curves as are expressed by the general equation:

$$G_m \cdot (Q - L)^n = \text{const.},$$

or whether they are only curves, of which the end-branches are hyperbolic curves.*

It is not difficult indeed, to understand that it is only essential *for the existence of the law* of corresponding states for the crystallization process, that the precipitation curve of *every* substance should cover the whole range of crystal dimensions between zero and $+\infty$.

Both theoretically and practically, the problem is a very interesting and very important one, to find such factors or such a factor implied in the crystallization process, of which the *mere equality* of values for *all* solid substances, irrespective of their chemical composition, would permit us to obtain, after the *complete* end of the crystallization process, precipitates *altogether identical* with regard to the *mean* magnitude (G_m) of the crystals these precipitates are made of.

The solution of this problem depends on our solving another question—the question as to what quantities play the parts of crystallization resistance and crystallization pressure in the formula for W:

$$W = k \cdot \frac{\text{crystallization pressure}}{\text{crystallization resistance}}.$$

Were we to consider the first period of crystallization *simply* as *vectorial* condensation of the molecules to extremely minute vectorial complexes (super-ultramicrocrystals or extremely small ultramicrocrystals), we could only arrive, in my opinion, by theoretical reasoning, at the extremely simple expression for W:

$$W_i = k_i \cdot \frac{Q - L}{L},$$

where $(Q - L)$ and L have the same significations as explained above, and k_i is a constant which, in a general way, is not the same for substances of a different chemical composition, of a different molecular weight, and so on.

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* It certainly depends on the kind of the equation of the curve, whether the mathematical formula of this law will be a simple or a complicated one.

But the first period of crystallization consists not *simply* in the *vectorial* condensation of molecules, this condensation being rendered complicated by other processes, *e.g.*, by the desolvation process of the molecules.

And generally, there are numerous factors which may actually affect the crystallization process (*e.g.*, in precipitations brought about by chemical reactions in solutions) as $(Q-L)$ progressively increases; our cause might thus be considered as theoretically hopeless, were it not possible to assume that all these factors are influencing the crystallization process in the same sense as does the increase or the diminution of the value of $(Q-L)/L$.

Under this latter assumption, however, we need but introduce into the ideal formula (W_i) for W, a certain *variable* multiplicator:

$$J = k_j \,.\, \left[\frac{Q-L}{L}\right]^m,$$

i.e.:

$$W = K\,.\,J\,.\,\frac{Q-L}{L} = K\left[k_j\,.\left(\frac{Q-L}{L}\right)^m\right].\,\frac{Q-L}{L} = \\ K\,.\,k_j\,.\left[\frac{Q-L}{L}\right]^n, \qquad \text{(III)}$$

where K is a constant which holds for all substances, and for all cases of precipitation of these substances, since all the differences, in chemical composition, in the molecular weight, and the like, will now receive due consideration by the factor k_j.

The following cases will of course be especially simple cases of crystallization: the case of precipitation of a substance of the same chemical composition from three (or more) solvents (the corresponding solubilities of this substance in the three solvents are L_1, L_2 and L_3); and the very simplest case will be the one when: $k_{j1} = k_{j2} = \ldots = k_{jn} = \ldots\ldots\ldots$ for all cases *to be compared* with each other and: $m = O$, in the formula for J.

It is clear that, if the precipitation curves from all three solvents are expressed by the equations:

$$\left.\begin{array}{l} G_m\,.\,(Q-L_1) = k'L_1\,; \\ G_m\,.\,(Q-L_2) = k'L_2\,; \\ G_m\,.\,(Q-L_3) = k'L_3\,; \\ \ldots\ldots\ldots\ldots\ldots\,; \end{array}\right\}$$

we shall have, for equal values of G_m:

$$\frac{Q-L_1}{L_1} = \frac{Q-L_2}{L_2} = \frac{Q-L_3}{L_3},$$

and, taking the ratio: $(Q-L)/L$ for a variable:

$$\left[\frac{Q-L}{L}\right].\,G_m = k'.$$

That is to say, the equilateral hyperbola with the coördinates G_m, $(Q-L)/L$ is, in this simplest case, the curve which, all at once, gives expression to the results obtained in precipitation from either of the three (or more) solvents.

It is not difficult to understand that, were the precipitation curves expressed by less simple equations:

$$\left.\begin{array}{l} G_m\,.\,(Q-L_1)^n = k_n L_1{}^n\,; \\ G_m\,.\,(Q-L_2)^n = k_n L_2{}^n\,; \\ G_m\,.\,(Q-L_3)^n = k_n L_3{}^n\,; \\ \ldots\ldots\ldots\ldots\ldots; \end{array}\right\}$$

the hyperbolic curve:

$$\left[\frac{Q-L}{L}\right]^n . \, G_m = k_n$$

would be the common expression of the results obtained in precipitation from either of the three (or more) solvents.

The most complicated * of the theoretically idealized cases is obviously the case when the equations of the precipitation curves are different in all three (or more) cases under consideration:

$$\left.\begin{array}{l} G_m\,.\,(Q-L_1) \;\;= k' L_1\,; \\ G_m\,.\,(Q-L_2)^p = k_p L_2{}^p\,; \\ G_m\,.\,(Q-L_3)^r = k_r L_3{}^r\,; \\ \ldots\ldots\ldots\ldots\ldots; \end{array}\right\}$$

In order to unite all kinds of precipitation results under one *single* hyperbolic curve, in a *special* case—an equilateral hyperbola—it is necessary to carry out a substitution of variables, *viz.*, to introduce the *variable* quantity:

$$N = J \, . \left[\frac{Q-L}{L}\right],$$

and then, all cases of precipitation may be expressed by the curve of the equation:

$$G_m \, . \, N = \text{const.}$$

If we compare the expression for N with the expression (III) for W we shall easily understand that, for the *theoretically idealized* cases, the assumption is made that, with equal initial values of W, the results of the crystallization process, with regard to the values of the magnitude G_m, are the same.

It should be well understood that the value of J in the variable N may vary, dependent on the precipitation conditions, from unity ($J = 1$) up to:

$$k_j \, . \left[\frac{Q-L}{L}\right]^m,$$

where m may be either zero, or unity, or, generally, any integer positive number.

We thus come to see that the initial value of W is of paramount importance for obtaining equal results in crystallization, and that whenever these values are *equal*, the values of G_m will also be equal for precipitates in different cases of precipitation.

No less important are the values of V (II), whenever the question arises as to the time intervals necessary for obtaining the above equal results in crystallization.

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* I do not class with the theoretically idealized cases the case, which is certainly quite conceivable mathematically, when:

$$J = k_j . \frac{(Q-L)m}{(L)m'}$$

where m is not equal to m'; see also later, in connection with the treatment of the real cases of precipitation.

For the sake of brevity, I shall confine myself to the treatment of the simplest of theoretically idealized cases, when the precipitation curves (see Fig. 1) are expressed by the equations:

$$G_m \,.\, (Q - L_1) = k'L_1;$$
$$G_m \,.\, (Q - L_2) = k'L_2;$$
$$G_m \,.\, (Q - L_3) = k'L_3;$$

In order to make ourselves a certain idea as to the mutual dependence between the numbers of crystalline germs (z) *spontaneously* arising in *unit* volume of the solutions and the magnitudes: $Q - L$ and L, we must go farther somewhat in our theoretical idealization of the precipitation processes.

Namely, we must assume that, in the precipitate obtained with a given value of $(Q - L)$, all crystals are equal, *i.e.*, that: $G_m = (Q - L)/z$, where $(Q - L)$ certainly signifies the amount of substance separated from unit volume.

Under this idealization, we have:

$$G_m \,.\, (Q - L) = k'L,$$

$$\frac{Q - L}{z} \,.\, (Q - L) = k'L,$$

$$z = \frac{(Q - L)^2}{k'L} = \frac{1}{k'} \,.\, \frac{Q - L}{L} \,.\, (Q - L);$$

that is to say, with constant values of $(Q - L)$, *i.e.*, with: $Q - L_1 = Q - L_2 = Q - L_3$, the number of the crystalline nuclei bears inverse ratio to L; *i.e.*, the smaller L the greater will be z, and the smaller G_m.

Therefore, for the precipitation curves in Fig. 1, we have:

$$L_1 > L_2 > L_3.$$

The distances between each other of these curves will be greater the greater the difference in solubilities.

If instead of $(Q - L)$ we take for the variable the ratio $(Q - L)/L$, we shall have, for all cases of precipitation which we are now examining, one single curve:

$$\frac{Q - L}{L} \,.\, G_m = k',$$

and with:

$$\frac{Q - L_1}{L_1} = \frac{Q - L_2}{L_2} = \frac{Q - L_3}{L_3},$$

$$z = \text{const.}\ (Q - L),$$

i.e., the number of spontaneously arising germs (*e.g.*, for the points: B_1, B_2, B_3, . . . , which belong to the same straight line, parallel to the horizontal coördinate axis) will be greatest in that particular case of precipitation, where, for the maintenance of the equality of the ratios: $(Q - L)/L$, the values of $(Q - L)$ is greatest.

Since, however, with equal values of the above ratio, we have, for instance:

$$\frac{Q - L_1}{Q - L_2} = \frac{L_1}{L_2},$$

it follows that the number of spontaneously arising germs will be greater, wherever the solubility of the substance is greater; and if:

$$\frac{L_1}{L_2} = 10, \text{ then there will be also: } \frac{z_1}{z_2} = 10.$$

Since the diffusion velocity is:

$$V = \text{const. } (C - L),$$

it will be clear that, supposing the values of "const." to be equal, the diffusion velocity will, for the case L_2, be ten times smaller, and the period of time necessary for crystallization to reach its end will correspondingly be longer.[5]

It is clear, therefore (see Fig. 1), that if, owing to the exceedingly small solubility of the substance, the precipitation curve has its larger portion lying within the ultramicroscopic domain, the preparation *by precipitation* of *large* crystals is only possible after the lapse of exceedingly great lengths of time, and under the application of uncommonly large volumes of the solutions, since with the volumes usually dealt with (*e.g.*, one litre), $(Q - L)$ is far too insignificant for obtaining crystals of appreciable dimensions.

Unfortunately, the lack of understanding of the correlations which here prevail is still inducing experimentalists to make fallacious inferences.

In an earlier place, I have already spoken of the fallaciousness of the "amorphy" doctrine which arose as a result of a similar misconception.

Let us revert once again to the precipitation curves in Fig. 1, to point out (this is quite clear from the above formula for W) that the higher the position occupied by these curves, the smaller is the value of W, with equal $(Q - L)$; *i.e.*, if this latter equality is maintained, we shall have:

$$W_1 < W_2 < W_3 < \dots\dots\dots$$

We have earlier treated the *simplest* of the theoretically idealized cases, viz., the case of the precipitation of the same substance from different solvents—under the tacit assumption that the energy by which the molecules of this substance are retained by the solvent is directly dependent on the solubilities.

The tendency toward spontaneous crystalline germ formation is certainly greater, the greater $(Q - L)$, and the smaller L, *other conditions being equal.*

For substances, however, which are of a different chemical composition, cases are thinkable when, with equal values $L_x = L_y$, the energies of retention of their molecules by the solvent will not be equal; an inequality of that kind is also thinkable, whenever the solubilities of the same substance in solvents which differ from each other in their chemical nature, approach each other.

Apart from this, in the case of substances of chemically composite nature, of which the molecules are voluminous, it is already sufficient that but a few (as compared with the case of chemically simple substances) such molecules should unite, in order to form a so-called "physical" boundary surface between the solvent and the substance separating therefrom, *i.e.*, in order to form a crystalline germ.

And this gives rise to such conditions, for the molecules loosely held by the solvent, of chemically composite substances (which, however, are still *relatively* well soluble over a certain temperature range), under which, even with not large $(Q - L)$, W becomes large; that is to say, very many invisible crystalline germs will arise; at the same time V (the diffusion velocity of growth of the germs) will be quite insignificant owing to the smallness of the diffusion coefficient; any attempt made to increase V by raising $(Q - L)$ would, in such cases, bring about further increase in number of the invisible crystalline germs.

In later parts of the present paper these cases will be treated at somewhat greater length, because of their importance for the understanding of the gelatinization process of the so-called reversible colloids such as gelatin, agar, and the like. If in the present connection attention has been called to them, this has merely been done to point out once again the influence exerted on the tendency toward spontaneous crystalline germ formation, by variables other than $(Q - L)$ and L.

It is hardly possible, and still less necessary, to give here a detailed treatment to all the variables which are likely to affect the spontaneous crystallization process.

As pointed out above, all these variables can most easily be classed in two groups according to the influence they exert on *spontaneous* crystallization; one of these groups would exert exactly the same action on spontaneous crystallization as would exert a simple increase of $(Q - L)$, or a simple reduction of L; the second group would produce the same effect as would a simple reduction of $(Q - L)$ or a simple increase of L; that is to say, the influence of these variables receives due consideration, being comprised in the above mentioned *variable* multiplicator J.

If viewed from theoretical aspects, there is another essential question demanding immediate decision—a question concerning the results obtained in precipitation of solid substances from solutions.

It would be interesting, indeed, to answer the question: what are the precipitation conditions under which *the same average number* of crystals of the *same mean magnitude* (G_m) (in gram-molecules) will form in unit volume for *any* given substance?

This can be realized in two distinct cases:

The first case will be the one, when we succeed discovering such solvents for two chemically different substances, X and Y, that, during crystallization from these solvents, at whatever moment of the processes, we should have:

$$W_x = W_y, \text{ and } V_x = V_y.$$

For obtaining such equal velocities it is necessary that, by changing the temperature, we should be able to secure, for the substances X and Y, an equal diffusion coefficient.

The second case—which is the most interesting for the theory of the colloid state—takes place with especially high values of W when namely the crystallization process is practically almost wholly completed during the *first* stage of crystallization.

If, to simplify our reasoning, we assume: $J_x = J_y$, it will then be necessary, for obtaining the results desired, that in the first instance:

$$\frac{Q_x - L_x}{L_x} = \frac{Q_y - L_y}{L_y},$$

the values of these ratios being extremely large; as, however, our possibilities are rather limited in preparing high Q (respectively—extremely high concentrations of the reacting solutions), the only way to follow would be selecting for our substances such solvents, in which the solubilities L_x and L_y would be exceedingly small.

If the L_x and L_y selected are really *vanishingly* small—and *equal,** then if, for instance, we carry out the synthesis of the substances: $X = A + B = AB$, and $Y = C + D = CD$, through mixing together equal volumes of reacting solutions of the substances: A, B, C, and D, of the same—exceedingly small—gram-molecular concentration, we must obtain, *practically instantaneously,* such suspensions (respectively—such colloid solutions) of very minute crystals of substances X and Y as would contain in unit volume the same *average* number of crystals of the same *mean* magnitude.

It goes without saying that, in order to establish this *average* number of crystals, we shall have to carry out a *sufficiently large* number of experiments, using the same concentration of the reacting solutions, and that only then this *average* number of crystals present in unit volume of the suspension (colloid solution) under investigation will be *proportional* (by no means equal) to the number of molecules (*Avogadro's* Number) present, under the same conditions, in unit volume of a true solution of the same gram-molecular concentration as that of the suspension (colloid solution) under investigation.

In other words, with the equality:

$$\frac{Q_1 - L_1}{L_1} = \frac{Q_2 - L_2}{L_2} = \frac{Q_3 - L_3}{L_3} = \ldots = \frac{Q_n - L_n}{L_n},$$

which is reached with *equal* and vanishingly small L $(L_1 = L_2 = L_3 = \ldots = L_n)$ and with sufficiently small † concentrations $[(Q_1 - L_1) = (Q_2 - L_2) = (Q_3 - L_3) = \ldots = (Q_n - L_n)]$, we shall obtain suspensions (respectively—colloid solutions) of crystals, of which the *mean* magnitude (in gram-molecules) and the *average* number present in unit volume will be the same for all substances, and the latter proportional to the so-called *Avogadro's* constant.

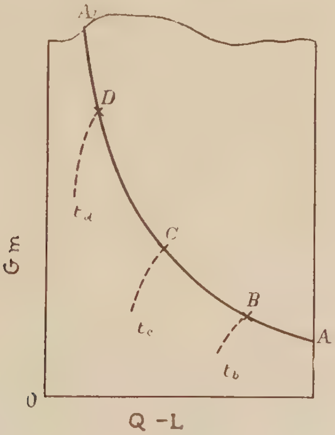

FIG. 2.

Let us now raise another question—the question as to the general form of the precipitation curves *antecedent* to the completion of the crystallization process.

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* It is self-evident that, since we assumed: $J_x = J_y$, all other conditions of precipitation must also be equal.

† With larger concentrations, the suspensions in real cases would prove unstable, unless additional conditions are fulfilled.

The precipitation curves drawn in Fig. 1 are those corresponding to the values of $(Q - L)$ after the end of the crystallization processes.

Of what general form * will be the precipitation curves, if the precipitation process is partially as yet incomplete?

This question is answered by the schematic curves in Fig. 2 and in Fig. 3.

Let (Fig. 2) the portions: ABt_b, $ABCt_c$, $ABCDt_d$, of the precipitation curve AA_1, be those corresponding to the time intervals: t_b, t_c, and t_d, as calculated, *e.g.*, from the moment of mixing together the reacting solutions; and let:

$$t_d > t_c > t_b.$$

During the interval t_b the crystallization process has only completed itself for the portion AB of the precipitation curve AA_1, but it is as yet incompleted in that portion of the curve which is higher than the point B; toward the end of the interval t_b the precipitation curve will accordingly have the form of curve t_bBA.

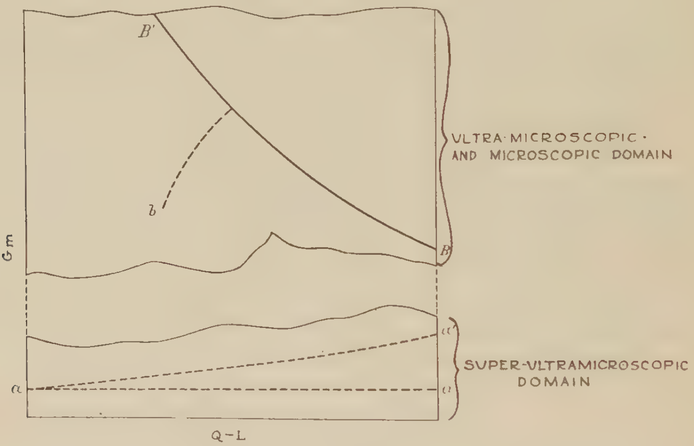

FIG. 3.

Quite similarly, at the end of the intervals t_c and t_d, the precipitation curves will be expressed by the curves t_cCA and t_dDA correspondingly.

Since, with $(Q - L)$ approaching zero, W and V will equally approach zero, it becomes evident that a *complete* precipitation curve is only obtainable, as hyperbolic curve, with infinitely small $(Q - L)$, if $t_n = \infty$

And herefrom it follows: 1. *Precipitation curves do fit into hyperbolic equations within those ranges only of $(Q - L)$ values, for which crystallization is altogether completed.* 2. *A complete hyperbolic precipitation curve can only be realized after the lapse of time $t_n = \infty$.* 3. *All incomplete precipitation curves possess a maximum in their left parts, which shifts upwards and to the left as t_n increases.*

At the zero moment, *i.e.*, the moment immediately following the pouring together of the reacting solutions (see Fig. 3), the particle (molecule) size in the supersaturated solutions will either be equal (the straight line $\alpha\alpha$) or, if we admit an association of molecules in proportion to concentration to take place, it will increase in proportion to the increase of $(Q - L)$ (the straight line $\alpha\alpha'$).

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* The equations of the curves of this kind are more conveniently treated in Section C of the present paper.

Then, after some time, crystallization begins; it first results in the precipitation curve Bb with a maximum, and subsequently, as soon as, *for this range of* $(Q - L)$ *values*, crystallization will be *altogether* completed—into the curve BB' which already represents a portion of a hyperbolic curve of the general equation: $G_m \,.\, (Q - L)^n = \text{const.}$

With this, I conclude my discussion of the fundamental precipitation laws for theoretically idealized cases, and shall now proceed to the consideration of the fundamental precipitation laws for actual real cases.

C. The Fundamental Precipitation Laws for Real Cases.

When proceeding from *theoretically idealized* to *real* cases of precipitation, it should be noted first, that the fundamental precipitation laws as deduced for the cases mentioned first, will play the rôle of so-called *limiting laws* for the latter, *i.e.*, the real cases.

This is an inference which follows from the fact that the real precipitation curves with the coördinates: G_m and $(Q - L)$ (for particulars: see below) fit into the general equation of the type:

$$G_m \,.\, (Q - L)^n = \text{const.}$$

with *only a certain degree of approximation;* a more exact analysis of the real precipitation curves proves that they are not exactly hyperbolic curves, but *curves with hyperbolic branches, i.e.*, curves, of which both the right-side and the left-side branches may be expressed with sufficient exactitude by the hyperbolic equation: $[G_m \,.\, (Q - L)^n = \text{const.}]$, and this not infrequently with different values of the constants for each branch.

For this very reason it occurs that, *e.g.*, the *law of corresponding states for the crystallization process*, while remaining, in its essence, wholly applicable to all real cases, forsakes in some of these cases, the simplicity of its mathematical expression.

It should further be noted that the velocity W—*i.e.*, the one prevailing during the first period of crystallization—is found to defy practical measurement: so, at least, it happens to be the case as matters actually stand with regard to our technical achievements, and to the available methods of measurement and observation.

As regards the velocity V—*i.e.*, the velocity during the second stage of the crystallization process—it may easily be measured in many a case of precipitation.

In no small a number of cases, however—and these are especially interesting to the synthesis of colloid systems—when this velocity proves also, either wholly insusceptible of measurement, or it may only be measured with the greatest difficulty.

This is why, in due time, I suggested the introduction, for studying real cases of precipitation, of a special coefficient N which I called the *"precipitate form coefficient"* or the *"dispersity coefficient."*

The expression of this coefficient is:

$$N = J \,.\, \frac{Q - L}{L} = J \,.\, \frac{P}{L},$$

where $Q - L$ is the amount of substance which must be deposited out from solution; in some cases it represents the initial supersaturation; L is the *ordinary* solubility of the substance, and J—an individual *variable* multiplicator, which is characteristic of the given precipitation process; J has here the same meaning as that in the formula for W discussed earlier in Section B.

For real cases, however, the assumption is made that, in the formula:

$$J = k_j \,.\, \frac{(Q - L)^m}{L^{m'}},$$

m' may as well not be equal to m; and besides, that both m and m' may not only be *integer* numbers greater than zero, but may also be *fractional* numbers greater than zero.

These assumptions will appear quite comprehensible to us, if we take into consideration that no experiment of ours, that was carried out under *real* conditions, could ever raise claims to be of an *absolute* exactitude.

Suppose now that we are given *any reaction whatever* for the preparation of some substance,* *e.g.*, the reaction:

$$AC + BD = \underset{\downarrow}{\underline{AB}} + BC.$$

Let this reaction be realized in some definite liquid media: *e.g.*, in water and in mixtures of water and ethyl alcohol.

Let us assume the solubility of substance AB to be greater in pure water than, *e.g.*, in 50 per cent alcohol; and the solubility of the same substance in this latter liquid, to be greater than it is, *e.g.*, in 85 per cent alcohol.

And now, let us prepare a series of reacting solutions (in terms of normal concentrations), pour them together (*equal* volumes of each of the two reacting solutions at one stroke), and then study the structure, and the changes in structure with lapse of time, of the resulting precipitates.

The greater the dilution of the reacting solutions, the greater (see Section A) must be the volumes taken for mixing them together; but, as a rule, there must always be *one* volume of one reacting solution poured into *one* volume of the other reacting solution.

If, on a "conventional" scale, we plot as abscissae the concentrations of the reacting solutions [*and not the* $(Q - L)$], and as ordinates the lengths [*and not the weights in gram-molecules of the crystals*] of the largest † crystals (*by no means of the aggregates of crystals*) present in each precipitate, as measured at definite intervals from the moment of mixing together the reacting solutions, we shall obtain the diagram given in Fig. 4.

The group of curves I will, *e.g.*, correspond to precipitation from purely aqueous reacting solutions; the group of curves II, to the case when reacting solutions in 50 per cent alcohol were applied for the precipitation of the substance AB; and the group of curves III, to precipitation from reacting solutions in 85 per cent alcohol.

From Fig. 4, what we realize first is that, as the solubility of the substance AB diminishes, the above groups of curves shift downward and to the left; that is to say, the group of curves I is located higher up and more to the right

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* *E.g.*, for the case of $BaSO_4$: $Ba(OH)_2 + H_2SO_4 = \underset{\downarrow}{\underline{BaSO_4}} + H_2O$; $BaI_2 + MnSO_4 = \underset{\downarrow}{\underline{BaSO_4}} + MnI_2$; and so on.

† The *"general character"* of the precipitation curves will obviously remain unchanged if we substitute for G_m the length of the largest crystals of the precipitate; and it is certainly *practically* easier to measure this latter (*i.e.*, the length) than to determine G_m. See reference 25.

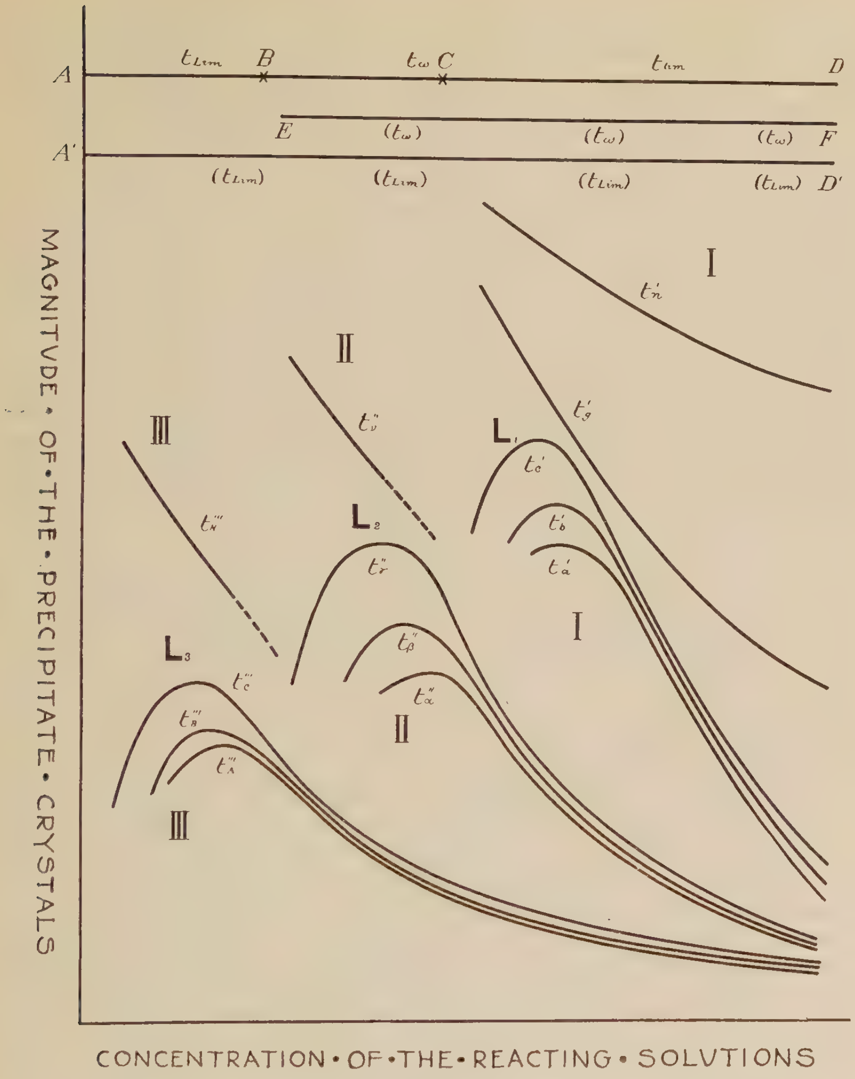

Fig. 4.

against the two other groups of curves; and the group of curves III is found lower down and on the left side of the groups of curves I and II.

Fig. 4 tells us further that each group of curves contains curves with maximum, as well as curves without maximum.

The first curve with a maximum, *e.g.*, that with the sign t_a' belonging to the group of curves I, corresponds to the end of a very short period of time elapsed from the moment of mixing together the reacting solutions (some 10-30 minutes)—just the time necessary for taking a sample, for microscopic investigation, of the precipitate, which had *practically* instantaneously arisen on mixing together the *relatively* concentrated reacting solutions.

After the lapse of time $t_b' > t_a'$, the magnitude of the precipitate grains will have already increased somewhat, as compared with the size attained toward the end of the period t_a'; and besides, there will already be precipitates present in the reacting mixtures of lower concentrations as well, which were able to appear toward the end of the period t_b'; the precipitation curve with the sign t_b' will therefore go somewhat farther in the leftward direction than did the curve with the sign t_a'.

At the same time, the maxima are displaced to the left, while the curves move up.

And after the lapse of the interval t_g', the precipitation curve will have no maximum * at all.

After the lapse of time $t_n' > t_g'$ the precipitation curve will already assume the position of the curve with the sign t_n'.

The displacement of the precipitation curves is produced by three kinds of processes: (1) direct growth of crystals at the expense of the molecularly-dissolved substance; (2) re-crystallization; (3) aggregation crystallization.

For theoretically idealized cases, we had assumed the two latter processes as non-existing; hence it follows that (compare Fig. 2), in real precipitation, we may only approach the theoretically idealized cases whenever the velocities of these two latter processes are *extremely small.*

For instance, if in our mind we bring to coincide with each other the right-side branches of the curves: t_g', t_c', t_b' and t_a', we shall obtain something that is near to Fig. 2; while it is worth noting that the abscissæ in Fig. 4 are concentrations of the reacting solutions, and not the $(Q - \dot{L})$ as was the case in Fig. 2; and the ordinates are crystal lengths, and not the values G_m.

In all the *real* cases of precipitation, the processes of re-crystallization and of aggregation crystallization are *always* taking place; accordingly, the precipitation curves will *always* be displaced, even after the end of *direct* crystallization, though sometimes very slowly.

The necessity of the re-crystallization process is to be recognized, apart from weighty theoretical considerations, on the ground that evidence has been afforded by *G. A. Hulett's* † experiments—experiments which are of paramount importance for the kinetics of formation and of disappearance of phases—of the solubility being greater of the smaller crystalline grains.

As regards the aggregation-crystallization process—a process which asserts itself with especial sharpness whenever very small (ultramicroscopic and super-ultramicroscopic) crystals come into touch with each other—its occurrence in real cases of precipitation has also been proved experimentally.

What then is the limit all precipitates strive to attain in the course of time? That is to say, *as time tends to become* ∞*?*

If, as a matter of agreement (see Section A), the same gram-molecular amount of precipitates of the substance AB is to be present, as result of precipitation, at the bottom of all vessels, whatever the concentrations of the reacting solutions used, then, for all three groups of curves, the limiting will be almost ‡ a straight line—AD—parallel to the axis of concentrations (see Fig. 4).

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* Only *practically:* in reality, there is still a maximum which only lies still farther to the left (concerning this question, see later).

† See Hulett's paper on this subject, this volume. J. A.

‡ Owing to re-crystallization (and to aggregation-crystallization, so far as very small crystals are concerned), the displacement of the precipitation curves can no sooner come to a standstill, than the whole amount of substance precipitated in each vessel has re-crystallized, so as to form *one single* crystal. If the reaction of preparation of the substance AB was some reaction of synthesis (*i.e.*, $A + B = AB$), all precipitates will then be present in a *pure* liquid, and all crystals arising therefrom, as ultimate limit of re-crystallization, will consequently be quite identical; and the limiting

Though the same straight line serves as a limit to all three groups of precipitation curves, the periods of time are far from being the same, which are necessary for each of the groups we are now investigating, to approach this limiting state *to an equal extent;* and if:

$$L_3 < L_2 < L_1,$$

then:.

$$t_{\text{Lim.}} > t_{\omega} > t_{\text{lim.}} \quad ;$$

which means that the *shortest* period will be the one corresponding to the case of the substance *AB* being present in the liquid medium, in which its solubility is *greatest, other conditions* (*i.e.*, for instance, with regard to diffusion, and the like) *being equal.*

It must at once, and most emphatically, be pointed out that the above periods: $t_{\text{Lim.}}$ t_{ω}, $t_{\text{lim.}}$ are of such a length that the limiting state can never be reached *practically.*

In view of the fact that, whatever the concentrations of the reacting solutions, crystallization commences, of course, with particles of molecular dimensions, the *first* precipitation curve (the one corresponding to the beginning of the first moment of the crystallization process) will also be *almost* a straight line coinciding (when plotted on the "conventional" scale we have adopted in Fig. 4) with the axis of the concentrations.

It thus happens that all the precipitation curves with the coördinates: "crystal length, concentration of the reacting solutions," while moving and undergoing deformations in the course of time, are contained between two straight lines as correspond to the times:

$$t_{\text{initial}} \text{ and } t_{\text{limiting}}.$$

It is not difficult to understand (see Fig. 5) that our subdividing the precipitation curves into curves with a maximum and curves without a maximum rests merely with the practical difficulties entailed by awaiting crystals to appear spontaneously from slightly supersaturated—which therefore keep supersaturated *for very much time*—solutions.

In Fig. 5, the domain of such slight supersaturations ($Q - L$) is marked on the axis of abscissæ by I; the mark III corresponds to supersaturations with which the spontaneous apparition of crystalline germs is *instantaneous* ($Q - L$—relatively large); and II marks the domain of the intermediate supersaturations, for which it is *practically* not difficult to await spontaneous apparition of crystalline germs.

If we look at the curves in Fig. 5 which are on the right of the vertical line Kn the *practical* discrimination between precipitation curves with a maximum and without a maximum will become comprehensible to us; if, on the other hand, we look at the curves in Fig. 5 "en bloc," we shall at once see that, in reality, the maxima are only moving leftward, to the end of the precipitation curves, while corresponding to concentration domains, which gradually become narrower and narrower, of the solutions applied for the reactions.

Let us now turn again to the three groups of curves given in Fig. 4.

line will, in this case, be *rigidly* straight and parallel to the axis of concentrations. But if the reaction of preparation of the substance *AB* was some reaction of double decomposition ($AC + BD = AB + BC$), there will be a second reaction product (BC) present in the mother liquor in varying concentration; and this will affect the habit (accordingly also the crystal length) of the crystals obtained as a result of re-crystallization (in this case, there will certainly be also but one single crystal of the same gram-molecular weight present in each vessel, after the complete termination of the crystallization process); for this very reason, the limiting curve is, in these cases, but an *almost* straight line.

Thus far, we have considered these groups as belonging to the same substance when placed under different conditions of precipitation—with different solubilities.

Quite in agreement with my experiments, however, we may also regard these groups of curves as belonging to three different substances: X, Y, and Z, with the solubilities: L_1, L_2 and L_3.

In this case, owing to the difference in density of the substances constituting the precipitates, the *limiting* curves with the coördinates: "crystal length, concentration of the reacting solutions" will, of course, no longer be able to coincide with each other; each curve will therefore have a position of its own: say CD—for the group of curves I; EF—for the group of curves II; and $A'D'$—for the group of curves III.

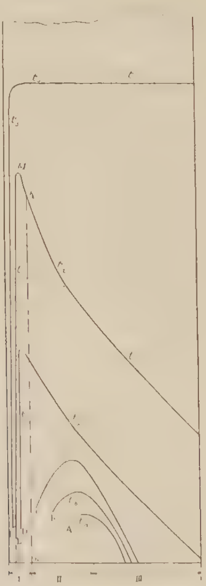

Fig. 5.

It was entirely deliberately that I abstained from giving any *fixed* scale in the scheme in Fig. 4, for either the concentration or the crystal length axes.

I insist repeating as strongly as I can that I did it intentionally, and precisely for the very distinct reason that *the general precipitation laws given expression by this scheme, will apply to substances of any solubility, and quite irrespective of whether the precipitate crystals of these substances can be descried with the naked eye, with the microscope, or with the ultramicroscope.*

But it is very important for the synthesis of colloid systems, for the clearing of the "mystery" of which *Thomas Graham* spoke (*loc. cit.*) about the transition from the "world of colloids" to the "world of crystalloids" and vice versa, that the scheme in Fig. 4 be given on some fixed scale, though plotted along the coördinate axes in a "conventional" manner.*

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* When using the proper manner of plotting, it is impossible to make the drawing explicit; this is why a "conventional" scale had to be adopted for the figures. Precipitation curves plotted on non-conventional scale will be given later.

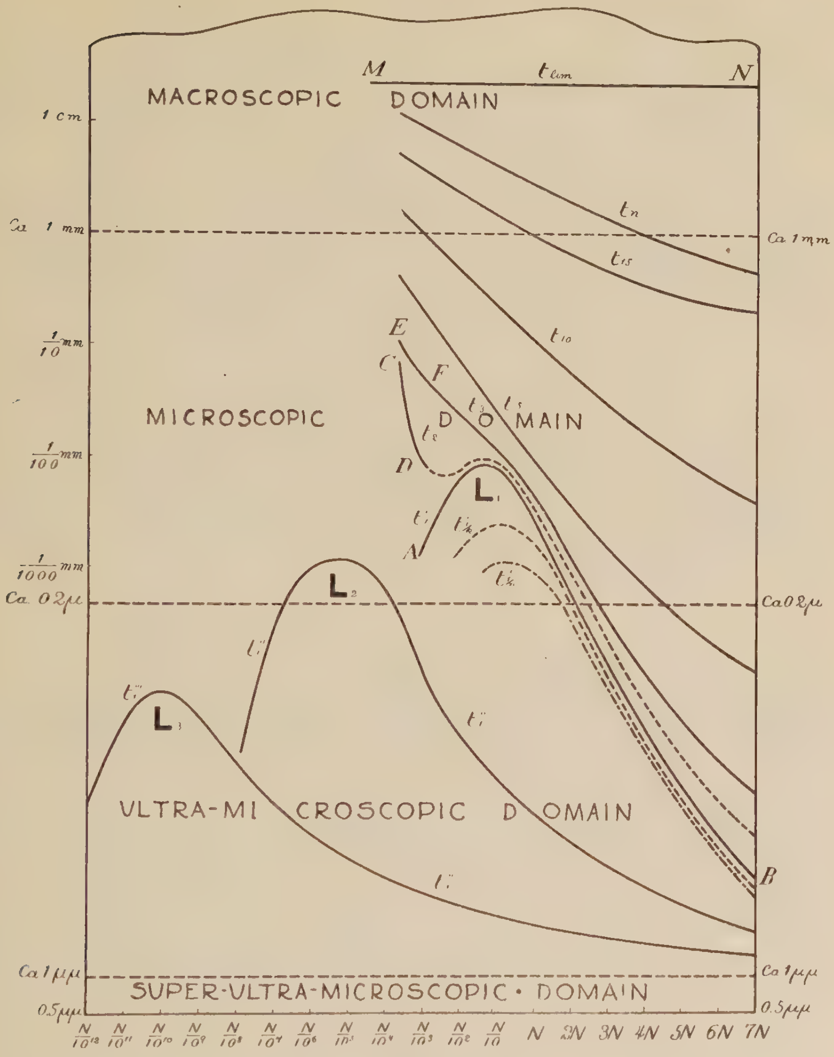

Fig. 6.

And this is what I did in Fig. 6.* (I ask the reader to pay no attention, for the present, to the curve Ct_2D.)

In the scheme Fig. 6 the abscissæ are concentrations of the reacting solutions, the coördinate center being taken not in zero concentration, but in the point corresponding to the concentration $N/10^{12}$ (normal concentration divided by ten in the twelfth power); along the ordinate axis the dimensions are plotted corresponding first to the superultramicroscopic (the coördinate center being taken about half-way between the extremes of the domain), then to the ultramicroscopic, the microscopic, and finally, to the *macro*scopic domains.

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* In order to simplify the scheme, all sets of curves without a maximum have been omitted except for the case of precipitation which corresponds to L_1.

In order to treat the precipitation curves in Fig. 6 on the base of a thorough understanding, it must be made clear, in what manner L in the formula of the dispersity coefficient:

$$N = J \, . \, \frac{Q - L}{L}$$

varies, as the concentrations of the reacting solutions prepared in some *definite* liquid undergo progressive increase.

Suppose we are given two reactions, *e.g.*, of the preparation of $BaSO_4$:

$$BaI_2 + MnSO_4 = \underset{\downarrow}{\underline{BaSO_4}} + MnI_2, \text{ and}$$

$$Ba(OH)_2 + H_2SO_4 = \underset{\downarrow}{\underline{BaSO_4}} + H_2O;$$

let both reactions be realized under application of aqueous reacting solutions.

In the case of the second reaction, the second reaction product is water; we therefore might expect that, on changing the concentration of the reacting solutions, Q would be alone to change in the formula:

$$N = J \, . \, \frac{Q - L}{L},$$

while L would remain constant during precipitation.

But it is not so. The fact of the matter is that, even in this apparently very simple case, L happens to be a quantity that "oscillates" about a certain medium value which corresponds to the solubility of large crystals of $BaSO_4$ in pure water.

However momentary the reaction of the formation of $BaSO_4$ may appear to us, it certainly requires, for its consummation, some definite amount of time, if ever so small; as to the time necessary for mixing together the reacting solutions, it can certainly by no means be classed as momentary.

And therefore, if *e.g.*, some definite volume of H_2SO_4 reacting solution is poured into an equal volume of $Ba(OH)_2$ reacting solution, the $BaSO_4$ will separate out, during the first period of its formation, in the presence of a certain excess of $Ba(OH)_2$ molecules;* if the reacting solutions are poured together in the reverse order, there will be, for some time, an excess of H_2SO_4 molecules.

These quantities present in excess (of barium hydroxide or of sulphuric acid) are varying as the concentrations vary of the reacting solutions, and the effect they produce on the solubility L will be different[6] for different concentrations.

Apart from this, heat is externated during the course of the reaction and during crystallization, which produces a change in temperature of the solution, and consequently makes also for an oscillation of the value of the solubility L.

In cases of reactions such as *e.g.*: $BaJ_2 + MnSO_4 = \underset{\downarrow}{\underline{BaSO_4}} + MnI_2$ the second reaction product (in the reaction quoted—MnI_2) will also affect the solubility L.

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* Or ions—to use the language of the ion theory.

Earlier in the text, I have already spoken on the influence exerted on solubility by the magnitude of crystals.

All the above enumerated decreases (or increases) of the solubility L depend, either directly or inversely, on the concentration of the reacting (respectively—of those formed after the completion of the reaction) solutions, and all of them receive consideration in the *variable* multiplicator J.

In some cases of the precipitation processes, the oscillations of L are insignificant; but in other cases, they may not only be noticeable, but even quite considerable.

It would generally be well to know two values of L during the course of the precipitation process, viz:—the value L_w, which corresponds to the moment of the spontaneous formation of crystalline germs, and L_v—the value after the termination of the reaction, *i.e.*, the solubility in presence of a second reaction product.

The value L_v is the one determining the velocity of the re-crystallization process, and generally, any changes in magnitude of crystals of a precipitate, while the precipitate is kept stored under the mother liquor.

The values of L_v can easily be determined experimentally; but the determination of the values of L_w is not so easy, for it implies the necessity of carrying out a systematic investigation on the effect produced on the crystal dimensions by different quantities of the reaction components present in excess.

L_w being the solubility of the substance during the *first* stage of crystallization, is very important inasmuch as it influences the structure of the precipitate in the initial period of its existence.

From what has just been stated concerning the oscillations, both during and after the process of precipitation, of the values of L—oscillations which, at that, would vary dependent on the concentrations of the reacting solutions, it will clearly be seen that, we may only expect our theoretical deductions, from their *quantitative* side, to be confirmed by experience—L being understood to signify, in the formula of N, the *solubility of large crystals in pure solvents*—if we are dealing with such cases of precipitation, in which the above oscillations obey, for different solvents and different substances, to the same quantitative laws.

If we succeed in discovering (see below) real cases of the above kind, this will be—open and explicit—a really splendid confirmation of the correctness of the foundations of the theory presented in Section B.

In the course of further discussion, let it be accepted that, in the formula of N, the letter L is to designate the *ordinary* solubility of large crystals in a given *pure* solvent; while also accepting that, throughout the whole set of experiments, the oscillations of L with increasing concentration of the reacting solutions, take place within such limits that, notwithstanding these oscillations, *the values of:*

$$N = J \cdot \frac{Q - L}{L}$$

will still increase progressively, as the concentration progressively increases of the reacting solutions.

I describe such cases of precipitation of substances as *normal* cases, to distinguish them from other cases of precipitation when, with the progressive increase of the concentration of the reacting solutions, N will now decrease, now increase, and now remain constant.

These latter cases of precipitation of substances are to be *designated* as *abnormal* cases.

For all normal cases, the precipitation curves are those given in Fig. 6.

For *abnormal* cases—dependent on how the value of N changes on changing the concentration of the reacting solutions—*e.g.*, one of the precipitation curves (II, III, a, b, IV) shown in scheme Fig. 7 may take place. (The curve with the signs I, I, I, represents the precipitation curve with a maximum, which corresponds to the normal case of precipitation.)

In my further discussions, I shall confine myself to a more detailed analysis of only the *normal* cases.

Let us get a deeper insight into the scheme in Fig. 6, which I called the scheme revealing the "mystery" about the transition of any substance from the "world of colloids" to the "world of crystalloids" and vice versa, and let us try to see what it tells us.

First of all—and this is all-important for the theory of the colloid state—the scheme tells us this much: if we bring any typical "crystalloid" desired under suitable conditions of precipitation, this "crystalloid" will turn out a typical "colloid," because, under these conditions, practically the whole of its precipitation curve will lie in the ultramicroscopic domain (*e.g.*, the curve $t_1'''L_3t_1'''$).

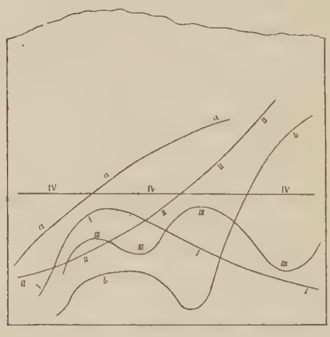

Fig. 7.

Reverse transition, *i.e.*, transition from "colloid" to "crystalloid," is also quite possible as the scheme in Fig. 6 indicates; because, under appropriate conditions of precipitation, the precipitation curves already lie, practically wholly, within the microscopic, or even the macroscopic domain.

If for a substance whose molecules are not excessively complex, we assume the values of J in the coefficient N to be practically equal for this substance precipitating from different media, then the transition will be regulated by the value of the magnitude L, the crystal dimensions being smaller, the smaller this value, with equal values of $Q - L = P$.

In Fig. 6: $L_1 =$ about 10^{-5} gram-molecules per one litre; $L_2 =$ about 10^{-8} gram-molecules per one litre; and $L_3 < 10^{-12}$ gram-molecules per one litre.

The curve L_1 corresponds, *e.g.*, to precipitation of $BaSO_4$ from aqueous reacting solutions, whereas the curves L_2 and L_3—from alcoholic-aqueous solutions; with an alcohol content exceeding 40 per cent, the precipitation curves for $BaSO_4$ are already, in their largest parts, in the ultramicroscopic domain, being located the lower and the more to the left, the greater the alcohol contents (*e.g.*, 75 per cent, 85 per cent) of the mixtures.*

Conforming to its position in the ultramicroscopic domain, the curve L_3 corresponds also to the precipitation curves for the hydroxide of aluminium—from aqueous reacting solutions; for NaCl and $CuCl_2$—from reacting solutions in *absolutely* dehydrated benzene, toluene, xylene, and so on.

Increasing the solubility of aluminium hydroxide by strong ammonia, and conducting the precipitation at an elevated temperature, suffice to cause the precipitation curve of even this typical colloid, partially to go over to the microscopic domain, since we shall already have beautiful microcrystals of $Al_2O_3 \cdot 3H_2O$; and so forth.

It is not difficult to understand that, with equal: $Q_3 - L_3 = Q_2 - L_2 = Q_1 - L_1$, it is for the curve L_3 that we obtain the largest values for:

$$N = J \cdot \frac{Q_3 - L_3}{L_3},$$

and that it is these extremely large (even with very small $Q_3 - L_3$) values of N that make the substance a typical "colloid," with *practically* its whole precipitation curve lying within the ultramicroscopic domain.

It is self-evident that no less enormous values of N can also be reached with relatively small values of $(Q - L)/L$, if under the conditions of precipitation, the values of J are sufficiently large.

Hence it follows that reduction of solubility is not the only means to effect the transition from "crystalloid" to "colloid," but that this can also be done in other ways, that would increase the values of J.

Solvation (as connected with molecular association), polymerization of the molecules, and complexity of the chemical composition of the molecules—these are the three outstanding factors leading to increase in the values of J; it is better, however, to treat these factors later on.

I shall now point out very briefly the influence of dust and of adsorption phenomena on the increase in value of J.

If the dust particles are able to produce (consequent on the adsorption process) a higher concentration of the solution at their surfaces, they increase the supersaturation $(Q - L)$, and provoke either a premature formation of crystals, or generally a formation of crystals in larger numbers than it would be the case if no dust were present; if with such an adsorption the dissolving capacity of the solvent is affected in the sense of the reduction of this capacity, then $(Q - L)/L$ will increase, and consequently, we shall have again an increase in number of spontaneously arising crystalline germs or nuclei.

If the substance of the dust is of such a nature that neither the supersaturation around its particles will increase, nor the solubility diminish, this kind of dust will be inactive for the crystallization process.

And the active dust will act quite in a similar way, as if no dust was present, but $(Q - L)/L$ would increase through either the increase of Q or the decrease of L; that is to say, the effect of active dust is duly taken into account by the increase of the value of factor J.

The curve Ct_2D in Fig. 6 is to demonstrate the above influence of dust on precipitation; if there were no influence of dust, or if it were strongly reduced, the precipitation curve would assume (after the lapse of time $t_3 > t_2$) the form EFt_3.

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* According to the work of Lobry de Bruyn on the solubility of salts in *absolute* solvents, the solubility of $BaSO_4$ in truly *absolute* alcohol may even be greater than its solubility in 95 per cent alcohol.

The presence in solution during precipitation of foreign molecules—*of molecules that would exert no influence on the solubility of the substance undergoing precipitation*—may only assert itself in the sense of adsorption (contamination) of the crystals during their growth.

Such contamination will at first (with some relatively small concentration of the foreign molecules) bring forth a distortion of the crystal form (*e.g.*, twisting, twinning, and so on, of the single individuals), and then (with higher concentrations of foreign molecules)—an increase in number of crystals spontaneously arising in unit volume of the solution, consequent on which (see Fig. 8) the precipitation curves will move in the downward direction, so that, at a sufficiently high concentration of foreign molecules, the whole of the precipitation curve may even sink below the line *nm*, thus entering the ultramicroscopic domain.

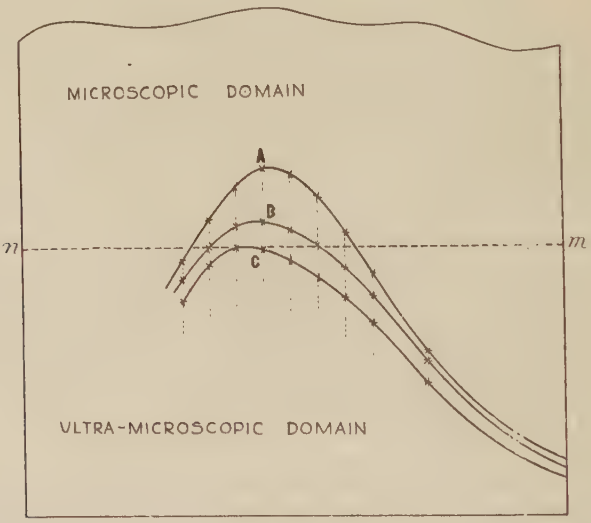


Fig. 8.

This is how, for instance, $BaSO_4$ precipitates from aqueous reacting solutions to which some gelatin or agar was added.[7]

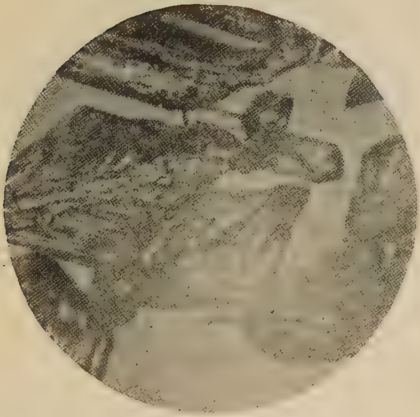
The above explained influence of adsorption or contamination on the crystals just forming turns out to be that, that it is just owing to this contamination of the growing surfaces of the crystals that the *local* (*i.e.*, near these crystals) increases of the supersaturation occur, giving birth to new crystals; that is to say, in the case we are now examining, the same takes place what might be obtained by simply increasing $(Q - L)$, *i.e.*, in the formula for N, the above explained influence of adsorption is also comprised in the factor J.

In all figures so far presented (Figs. 4-8), the precipitation curves have been plotted on a "conventional" (*i.e.*, a somewhat distorted scale; these figures were schemes, and not drawings).

Fig. 9 represents the precipitation curves properly plotted for the Ag_2SO_4 from 30 per cent alcoholic aqueous solutions.

PLATE IIa.

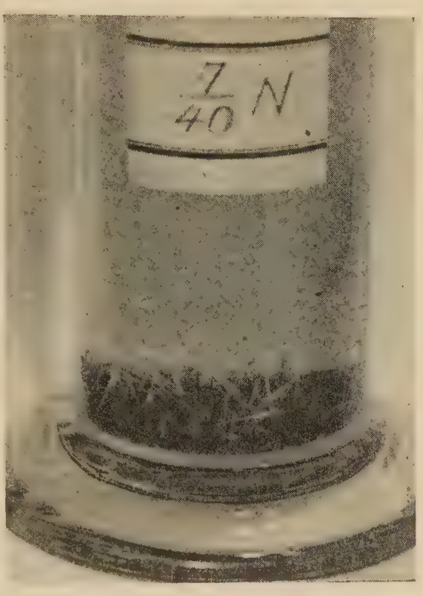
Ag_2SO_4 precipitates from aqueous reacting solutions.



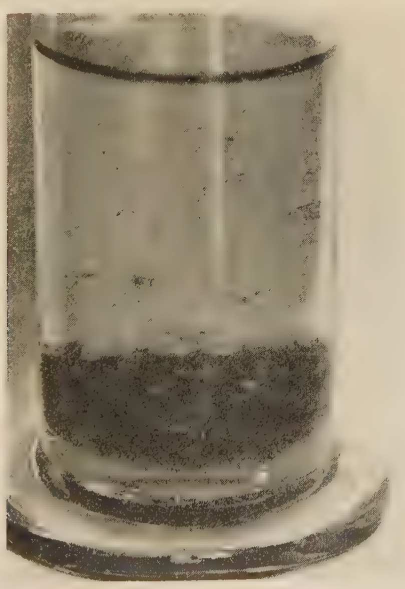
No. 9. Concentration of the reacting solutions 0.2 norm. Photograph taken about 1 hour after the formation of the precipitate. Magnification: about 115.

No. 9 bis. The same precipitate as in No. 9, but after 6 months' storage under the mother liquor. Magnification: about 220.

$AgCOOCH_3$ precipitates from aqueous reacting solutions.

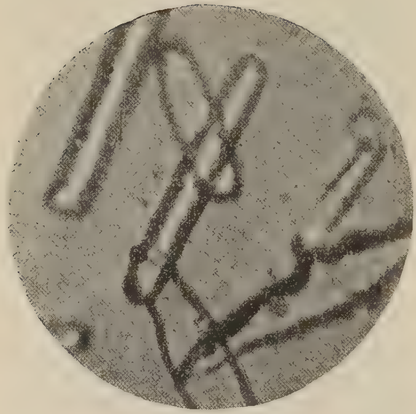


No. 12. Concentration of the reacting solutions 7/40 norm. Photograph taken after 2 weeks. 0.8 natural size.

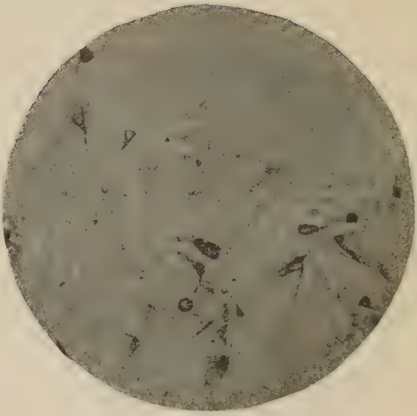


No. 13. Concentration of the reacting solutions 11/40 norm. Photograph taken after 2 weeks. 0.8 natural size.

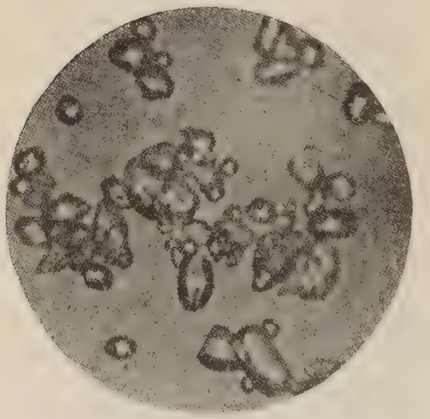
PLATE IIb.



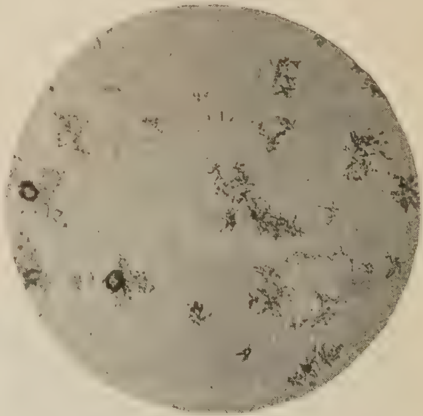
No. 10. Concentration of the reacting solutions 1 norm. Photograph taken 6 months after the apparition of the precipitate. Magnification: about 400.



No. 14. Concentration of the reacting solutions 3/5 norm. Photograph taken after 2 weeks. Magnification: about 25.



No. 11. Concentration of the reacting solutions 6 norm. Photograph taken 6 months after the apparition of the precipitate. Magnification: about 400.



No. 15. Concentration of the reacting solutions 1 norm. Photograph taken after 2 weeks. Magnification: about 60.

Analogous precipitation curves are also obtained for Ag_2SO_4 from aqueous and 60 per cent alcoholic-aqueous solutions,[8] and certainly for all *normal* cases of precipitation in a general way.

A vivid portrayal of how the dimensions of the crystals *diminish* with *increasing* concentration of the reacting solutions is offered in Plate II, where photographs and microphotographs are reproduced of precipitates of silver acetate [9] (Nos.: 12-15) and silver sulphate (Nos.: 9-11) which were prepared by precipitation from aqueous solutions at room temperature.

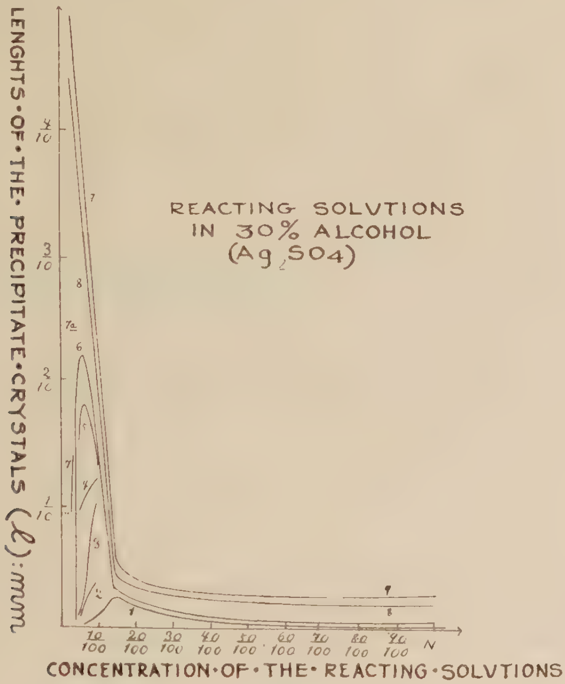


FIG. 9.

Curve 1: The solid phase appears practically instantaneously; the measurements of the crystal size have been made at the end of the time period T_o, which represents the period (about 10-15 minutes) required for the operations of sampling and photomicrographing.

Curve 2: $T_o + 5$ min.; Curve 3: $T_o + 10$ min.; Curve 4: $T_o + 20$ min.; Curve 5: $T_o +$ 40 min.; Curve 6: $T_o + 1$ hour; Curve 7: $T_o + 3$ hours; Curve 7a: $T_o + 24$ hours; Curve 8: $T_o + 2$ months; Curve 9: $T_o + 6$ months.

From Figs. 4, 6 and 9, which are nothing else than simple representations—schematic or exact (Fig. 9)—of experimental data, and which accordingly, contain nothing of any theories, it is easy to formulate altogether real precipitation laws, for all the *normal* cases of precipitation, which would establish the correlation between the size of the grains (of the crystalline individuals, not of aggregates of such individuals), the concentration of the reacting solutions, and the time periods elapsed from the moment of mixing together these solutions.

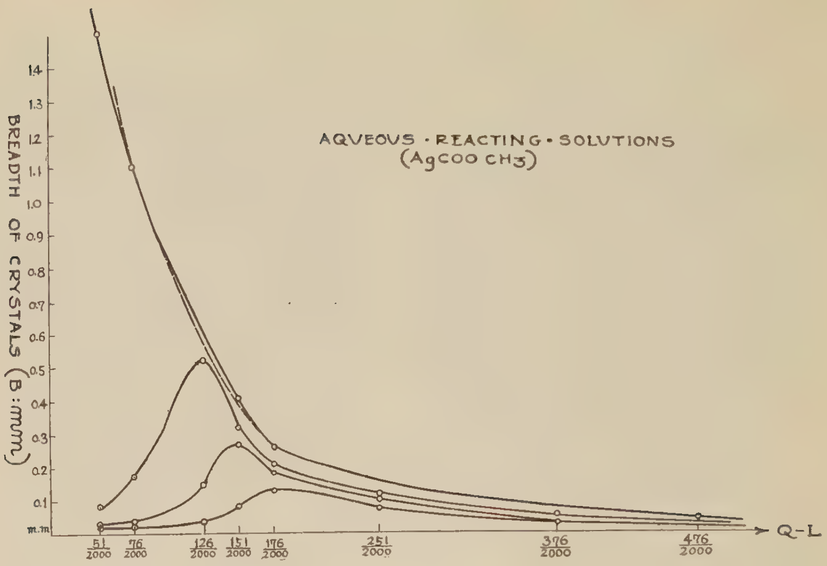


FIG. 10.—First curve with maximum: $-T_0$; Second curve with maximum: $-T_0 +$ 10 minutes; Third curve with maximum: $-T_0 + 1$ hour; Fourth curve without maximum: $-T_0 + 2$ weeks.

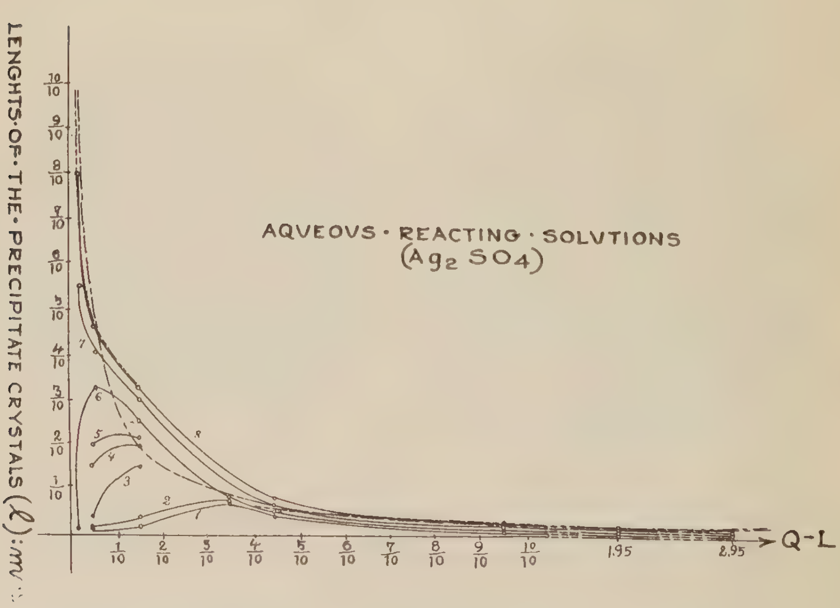


FIG. 11.—Curve 1: $-T_0$; Curve 2: $-T_0 + 5$ min.; Curve 3: $-T_0 + 10$ min.; Curve 4: $-T_0 + 20$ min.; Curve 5: $-T_0 + 40$ min.; Curve 6: $-T_0 + 1$ hour; Curve 7: $-T_0 + 2$ months; Curve 8: $-T_0 + 6$ months.

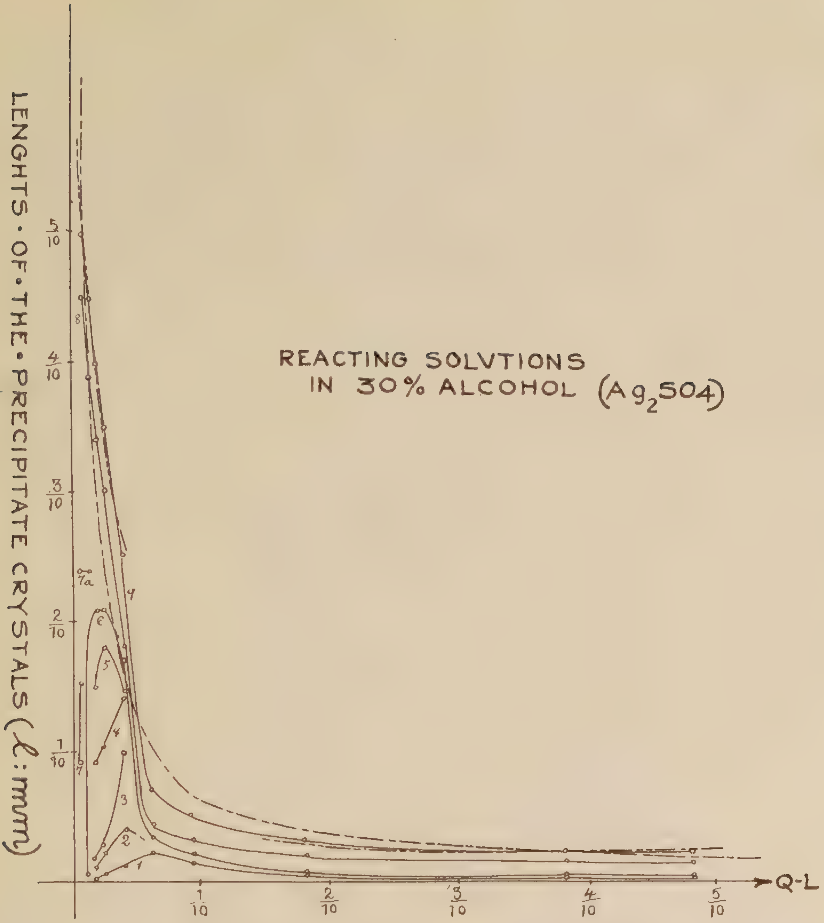


FIG. 12.—Curve 1: — T_o; Curve 2: — $T_o + 5$ min.; Curve 3: — $T_o + 10$ min.; Curve 4: — $T_o + 20$ min.; Curve 5: — $T_o + 40$ min.; Curve 6: — $T_o + 1$ hour; Curve 7: — $T_o + 3$ hours; Curve 7a: — $T_o + 24$ hours; Curve 8: — $T_o + 2$ months; Curve 9: — $T_o + 6$ months.

I shall confine myself to only the formulation of those laws which are of *practical* value; these laws run as follows:

1. For periods of time smaller than that which is necessary for the completion of the processes of *direct* growth of crystals in *practically all* the solutions, even the slightly supersaturated ones: *The precipitation curves with the coördinates, "concentration of the reacting solutions, crystal magnitude"* *

---

* The *general* appearance of the curves will suffer no alteration, of course, if we plot as ordinates the weights of the precipitate crystals or G_m, instead of their lengths. In other words, the precipitation curves may, in this case, also be subdivided into curves with a maximum (the maximum is certainly not bound to remain at the same place as before) and curves without a maximum, and the like. In the present connection, it is worth noting that Sven Oden, availing himself of his beautiful registering apparatus, was able to determine the so-called "distribution curve" also for the $BaSO_4$, about which he states as follows: ". . . they furnish us with an example to von Weimarn's law that, with diminishing concentration of the reacting solutions, the masses of the particles (or the equivalent radii) increase." (*Koll. Zeitschr.*, 26, 100-121 (1920).)

are curves with a maximum; the greater the periods of time to which the curves correspond, the higher and the more to the left will be the maximum point of the curve.

2. For periods of time equal to or larger than that which is necessary for the completion of the processes of *direct* growth of crystals in *practically all* the solutions, even the slightly supersaturated ones: *The dimensions of crystalline grains decrease as the concentration of the reacting solutions increases.*

I shall not be detained here by the question as to the equations by which the curves representing these two laws could be expressed, for its solution will become quite clear as soon as we shall have answered the same question with regard to precipitation curves with the coördinates, "crystals length l, $Q - L$."

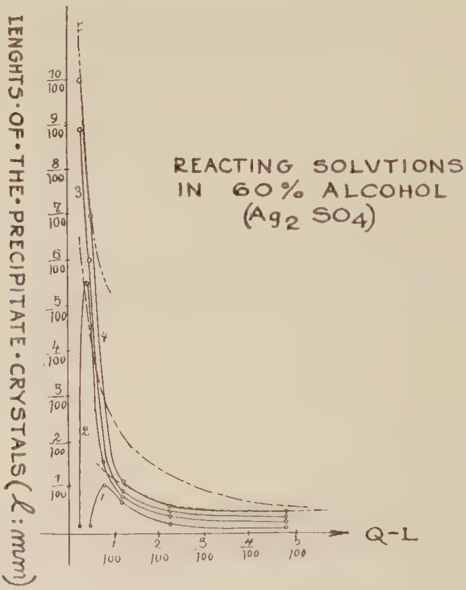


FIG. 13.—Curve 1: $-T_0$; Curve 2: $-T_0 + 1$ hour; Curve 3: $-T_0 + 1$ week; Curve 4: $-T_0 + 1$ month.

No great play of imagination is required to see that, were we to plot along the axis of abscissas, not the concentrations of the reacting solutions, but $(Q - L)$, taking the coördinate center at the point: $Q - L = O$ and $l = O$, the general character of the precipitation curves would not be altered (Figs.: 10, 11, 12 and 13), and only the wording of the above formulated precipitation laws would be a different one; so, for instance, the *second* law would run as follows: *The dimensions of crystalline grains decrease as $Q - L$ increases.*

Since $Q - L$ is a quantity altogether susceptible of real measurement, it follows that the formulation just quoted of the second law is also free of any element of theory.

In Fig. 10 the precipitation curves (with the coördinates: $Q - L$, b, crystal breadth) are given for the case of silver acetate under application of aqueous reacting solutions ($KCOOCH_3 + AgNO_3$); the Figs.: 11, 12 and 13 represent the precipitation curves of silver sulphate ($AgNO_3 + MnSO_4$)

from aqueous, 30 per cent, and 60 per cent alcoholic aqueous solutions correspondingly; in Figs. 11-13 the coördinates are: l—length of crystals, and $Q - L$.*

For the quantitative test of the theory explained in Section B, we are to select such cases of precipitation, for which the recrystallization and aggregation processes are as slow as possible, so that the errors committed in measurement be not too big.

The processes of recrystallization and of aggregation may be slow in two distinct cases: first, when the substance of the precipitate is truly negligibly slightly soluble; second, when the crystals constituting the precipitates are not below the microscopic size (the solubility must then not be vanishingly small).

The second case offers greater convenience for its quantitative study, for it is very difficult, when dealing with very fine-grained precipitates, to execute measurements of the ultramicrocrystals constituting these precipitates, with any approach to accuracy.

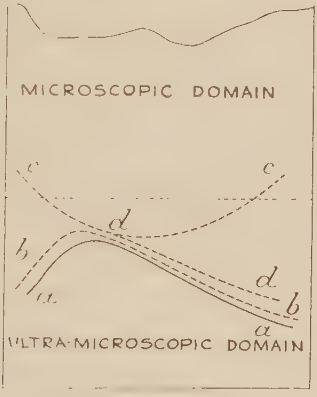


FIG. 14.

In order to evaluate and to understand these difficulties, a few words must be said about the formation of *aggregates* [10] or *aggregate-particles* in the precipitates, out of the extremely small ultramicrocrystals, and about the influence of this formation on the "apparent" deformation of the precipitation curve.

In the scheme Fig. 14, the precipitation curve *aa* represents a real precipitation curve with the coördinates: $Q - L$ and G_m; as always, G_m relates here, not to *aggregate*-crystals, but to compact *individual*-crystals.

After the lapse of a certain time, this curve will show noticeable deformation, and will first assume the positions *bb* and *cdd*, owing to the direct growth of the crystals and, in part, owing to the recrystallization process.

---

* The calculations of the concentrations were carried out in normal equivalents, and not in gram-molecules; for the silver acetate, the normal equivalent and the gram-molecular concentrations certainly coincide. It must be noted here (for particulars, see: P. P. von Weimarn, S. Otsuka and H. Hori, *loc. cit.*) that similar precipitation curves are also obtained for the lengths of $AgCOOCH_3$ crystals and the breadths of Ag_2SO_4 crystals (in this latter case, there was observed, with large $Q - L$ a second, gently sloping, small maximum, which can be explained by the changes in form of the grains: from long and thin to thick and short comparatively. The equations of the precipitation curves, *e.g.*, those for the breadths and those for the lengths, differ only in regard to the values of the constant; that is, *e.g.*, for $AgCOOCH_3$ we shall have for the breadth (b), as well as for the length (1) the following equations of precipitation curves: $b.(Q - L)^2 = k_b$, and $1.(Q - L)^2 = k_1$.

If the individual crystals are small ultramicrocrystals, it will then be impossible to distinguish, even with the ultramicroscope, to say nothing of the microscope, between an aggregate and a compact particle (a crystalline individual).

And therefore, if all the precipitation curves: *aa, bb,* and *cdd,* lie, with their largest parts, within the ultramicroscopic domain, there takes place, owing to aggregation [11] of the ultramicrocrystals resulting into the formation of aggregate-particles, an "apparent" deformation of the precipitation curve *cdd* to a curve of the form *cdc;* while, starting with the point *d*, the "apparent" sloping up of the curve is due to the fact that the aggregate particles on the right of point *d* were erroneously held for compact ones.

It is certainly true that such mistakes can always be detected by either the dispergation method of precipitates to colloid solutions (see below), or by examining the precipitates with X-rays (see below); but anyhow, it sometimes requires a great deal of work, to make an exact determination of the dimensions of compact particles in such precipitates.

The contraction of aggregate particles, the growing together of the individual ultramicrocrystals constituting these particles, and the rebuilding, with time, of the aggregates to more or less homogeneous crystals—all these processes are influenced by a number of factors (*e.g.,* the pressure exerted by the upper column of the precipitate on its lower layers; the presence of aggregators [see below], and the like) which, during the course of direct growth of compact crystals from solutions, are of no particular importance.

This is why, on submitting the theory of precipitation to a quantitative test, one preferably uses precipitates not excessively fine-grained.

This, however, is only a matter of expediency. In point of fact, we can always make the aggregation process—which, with slightly soluble substances, is generally sluggish—become so slow that it will prove no hindrance to our quantitative measurements.

The solubilities in water at 25° C.; of $AgCOOCH_3$ (0.062 gram-molecules in one litre of the solution) and of Ag_2SO_4 (0.025 gram-molecules in one litre of the solution) are not small enough that we might obtain excessively fine-grained precipitates; and besides, the solubilities of these substances may easily be lowered, as one wishes, *without any complications whatever,* by adding ethyl alcohol to the water.

Apart from this, the $AgCOOCH_3$ offers a somewhat special interest as a substance that crystallizes in strongly *negative* crystals.*

In Figs. 15, 16 and 17, I am giving several sets of curves with maxima; the equations which express these curves [12] are given below each figure.

To compare the curves in these figures with those in Figs. 10, 11, 12 and 13 will be enough to understand the possibility of expressing the precipitation curves by analogical equations.

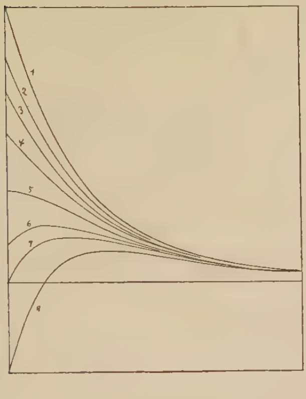
Without going into detail, I wish merely to point out that the equation of the type:

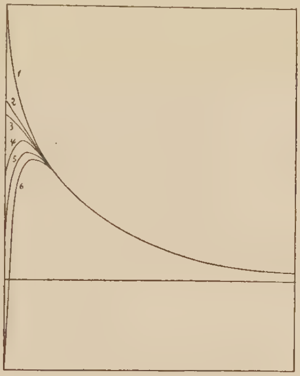
$$l\,.\,P^{n_1}\left(e^{\frac{k_2}{T\,.\,Pn}{}^{2}}-1\right)=k_1,$$

---

* This form of crystals, *i.e.,* the form of needles, remains with the $AgCOOCH_3$ precipitates even when the reaction of formation of this substance is realized in 95 per cent ethyl alcohol. Many of the $AgCOOCH_3$ precipitates obtained by the reaction in 95 per cent alcohol are extremely voluminous and display a *gelatinous*-flaky character.

My ultramicroscopic investigations (with Prof. Siedentopf's "Wechselkondensor") of these precipitates (Apochr. 58, Compens. ocul. 15, magnification 870) have shown the crystalline grains to be microscopic needles, whereby, in some of the precipitates submitted to examination, the width and the thickness, *but not the length,* of these needles were of ultramicroscopic dimensions.





$$y = a_1 c^{-c_1 x} \pm a_2 c^{-a_2 x}.$$

FIG. 15.

1. $y = e^{-x} + 0.5e^{-2x}$.
2. $y = e^{-x} + 0.2e^{-2x}$.
3. $y = e^{-x}$.
4. $y = e^{-x} - 0.2e^{-2x}$.
5. $y = e^{-x} - 0.5e^{-2x}$.
6. $y = e^{-x} - 0.8e^{-2x}$.
7. $y = e^{-x} - e^{-2x}$.
8. $y = e^{-x} - 1.5e^{-2x}$.

FIG. 16.

1. $y = e^{-x} + 0.5e^{-10x}$.
2. $y = e^{-x}$.
3. $y = e^{-x} - 0.1e^{-10x}$.
4. $y = e^{-x} - 0.5e^{-10x}$.
5. $y = e^{-x} - e^{-10x}$.
6. $y = e^{-x} - 1.5e^{-10x}$.

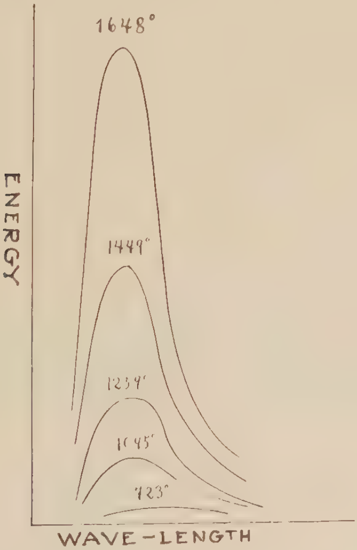


FIG. 17.

Equation:

$$E = k_1\lambda^{-5}\left[e^{\frac{k_2}{\lambda T}} - 1\right]^{-1} \text{ (\textit{Planck's} formula)}$$

and, as limiting case of the same:

$$E = k_1\lambda^{-5}e^{-\frac{k_2}{\lambda T}} \text{ (\textit{Wien's} formula) ; } E = k_1 T\lambda^{-4}e^{-\frac{k_2}{\lambda T}} \text{ (\textit{Rayleigh's} formula).}$$

(where: $P = Q - L$, and T—the time intervals elapsed from the instant of mixing the reacting solutions), which, with corresponding values of T and P, goes over into the equation:

$$l \,.\, P^{n_3} = \text{const.},$$

may successfully be applied for the expression of precipitation curves in general.

In the present paper we are especially interested in curves without maxima.*

As regards such precipitation curves for the case of silver acetate, we may see from Fig. 10, in which the dotted curve is that of the equation:

$$b \,.\, (Q - L)^{1.9} = k_b,$$

that the experimental precipitation curve approaches very closely the equation:

$$b \,.\, (Q - L)^2 = k_b;$$

exactly the same result has also been obtained for the length of crystals, and the equation:

$$l \,.\, (Q - L)^2 = k_1$$

expresses the experimental results with sufficient exactitude.

But so good an agreement is not always met with.

In the case of $AgCOOCH_3$ (see: Plate II, Nos.: 12-15) the crystals have the same form of needles with all concentrations; they change in size, not in form or in contours; but it is not the same with the Ag_2SO_4 (see: Plate II, Nos.: 9 bis, 10 and 11) for which the contours of the crystals vary with sufficient sharpness.

As can be seen from Figs. 11, 12 and 13 † (the dotted curves are those of the equation:

$$l \,.\, (Q - L)^{\frac{1}{1.2}} = \text{const.}),$$

the curves of the equation:

$$l \,.\, (Q - L) = k_1 \ddagger$$

do not coincide sufficiently well with the curves obtained from experiments.

But the right and the left branches of the precipitation curves, for the aqueous, as well as the alcoholic-aqueous solutions, can excellently be expressed (see, in Figs. 11, 12 and 13, the dotted curves which practically coincide with the branches of the experimental curves) by curves of the equation of the general type:

$$l \,.\, (Q - L)^{\frac{1}{3}} = \text{const.},$$

the values of the constant being not the same in the left and in the right branches of the curves.

In the case we are just considering, conformedly to the sharp changes undergone by the contours of the crystals, as the concentration of the reacting solutions progressively increases, the experimental curve breaks up into three parts, of which each may be sufficiently well expressed by hyperbolic equations of its own.

---

* Or in curves of which the maximum is too high and too much on the left for their *practical* realization under the conditions usual in laboratory work with regard to time periods, and under application of ordinary volumes of the reacting solutions.

† In the case of 60 per cent alcohol, the last experimental curve corresponds to the time of *one month only*, and not of 6 months, as for the case of water and 30 per cent alcohol. It is important that this should be borne in mind.

‡ Quite the same holds for the breadth of crystals.

I am now approaching the most interesting moment, in the sense of the concordance between the laws for the theoretically idealized and the real cases of precipitation.

In Fig. 18 the precipitation curves of Ag_2SO_4 (for the aqueous and the 30 per cent alcoholic-aqueous solutions—after 6 months, and for the 60 per cent alcoholic-aqueous—after 1 month) are given with the coördinates: $Q - L$ and l; and in Fig. 19—with the coördinates:

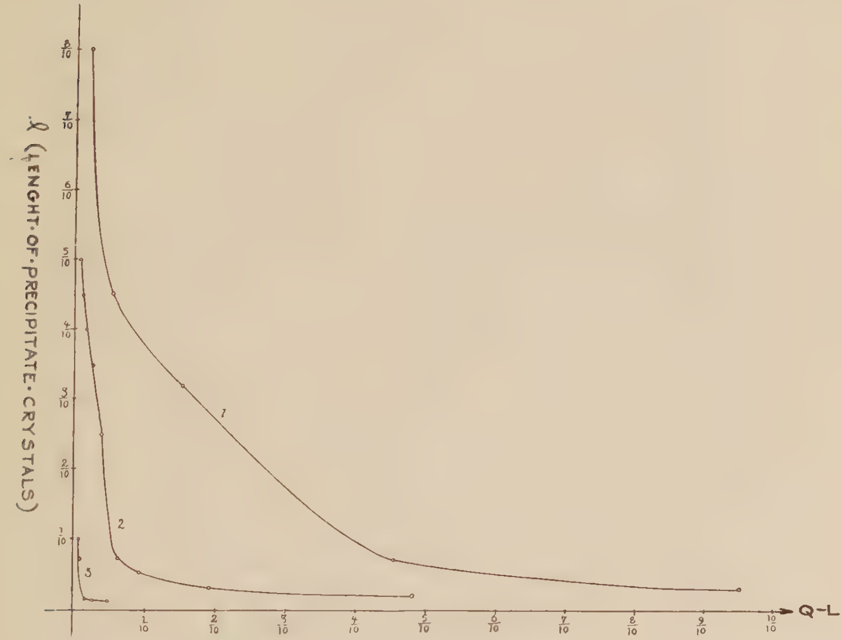


FIG. 18.—(Precipitation curves for Ag_2SO_4).

Curve 1.—Aqueous reacting solutions; the crystals have been measured after 6 months from the moment of mixing the reacting solutions.

Curve 2.—30% ethyl alcohol reacting solutions; the crystals have been measured after 6 months from the moment of mixing the reacting solutions.

Curve 3.—60% ethyl alcohol reacting solutions; the crystals have been measured 1 month after the mixing of the reacting solutions.

$$\frac{Q-L}{L} \text{ and } l.$$

For the reader who understands how many factors were influencing the precipitates of Ag_2SO_4 while these precipitates were kept for half a year under the mother liquor, the curve in Fig. 19 cannot but offer a wonderful experimental confirmation to the theory of the processes of precipitation, the theory explained in Section B. (The points corresponding to crystallization from 60 per cent alcohol are somewhat on the outside of the curve as it was drawn; but it should be noted that in this case the measurement of crystals was made after one month only, and not after 6 months.)

And thus we may say that *whenever the precipitation curves of substances from different solvents are subordinated to analogous laws, then, by substituting the coördinate*

$$\frac{Q-L}{L}$$

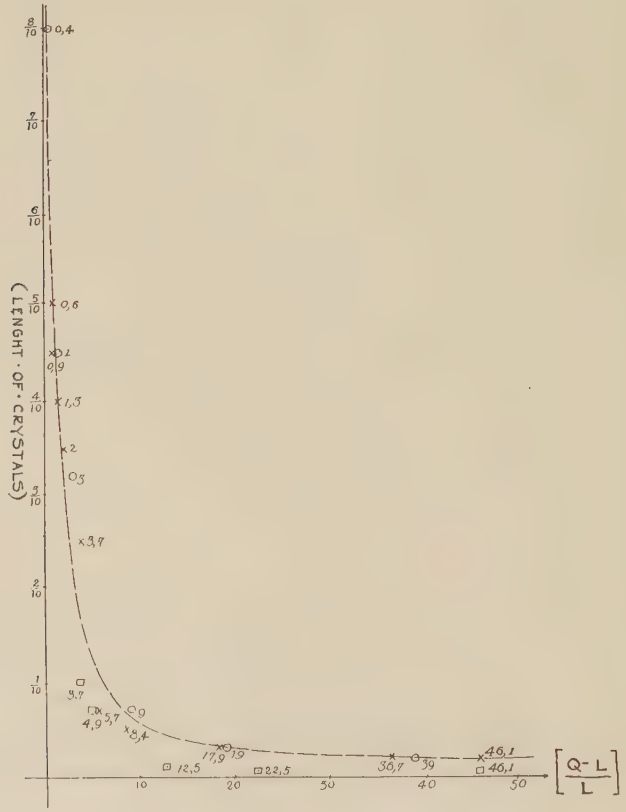


FIG. 19.

⊙—Crystals obtained from aqueous reacting solutions; measured 6 months after mixing the reacting solutions.

×—Crystals obtained from reacting solutions in 30% ethyl alcohol; measured 6 months after mixing the reacting solutions.

⊡—Crystals obtained from reacting solutions in 60% ethyl alcohol; measured 1 month after mixing the reacting solutions.

for the coördinate Q — L, the precipitation curves approach each other, almost to coincide, and sometimes actually coincide in a number of points.

This is the *real* law.

The theoretically idealized, limiting law (Section B) *exacts a complete coincidence of the precipitation curves in the case just treated.*

We can avail ourselves of this law [13] for determining with some approach to accuracy (sometimes but very roughly) the solubility of a substance in different solvents.

Thus, for instance, in the above treated case of Ag_2SO_4, the common expression of the precipitate form coefficient for all three cases will be:

$$N = q \cdot \frac{Q - L}{L},$$

the value of q being the same in all three cases.

For water we have:

$$G_m = \frac{K}{N_w},$$

where N_w is the precipitate form coefficient for water, and K—a constant, and for 30 per cent alcohol:

$$G_m = \frac{K}{N_A},$$

where N_A is the precipitate form coefficient for 30 per cent alcohol, and K —a constant, of which the value is the same as for water.

Suppose we know L_w, and let our unknown be L_A; with equal G_m we have:

$$\frac{K}{\mathrm{N}_w} = \frac{K}{N_A}, \text{ or: } N_w = N_A;$$

accordingly:

$$q \cdot \frac{Q_A - L_A}{L_A} = q \cdot \frac{Q_w - L_w}{L_w},$$

whence:

$$L_A = \frac{Q_A \cdot L_w}{Q_w}.$$

In the case of Ag_2SO_4 the agreement between L_A calculated and determined analytically proves to be rather satisfactory (*e.g.*: $L_A = 0.009$ and 0.007 gram-equivalents, as calculated against $L_A = 0.01$, as found analytically).

The fact that the precipitation curve for Ag_2SO_4, though not the whole of it, is very well expressed by the equation:

$$l \cdot (Q - L)^{\frac{1}{3}} = \text{const.}$$

proves that the simplest of the theoretically idealized cases of precipitation (Section B):

$$G_m \cdot (Q - L) = \text{const.}$$

is not a theoretical fiction.

And so, *the real precipitation curves without a maximum can be expressed: either, as a whole—by an equation of one single hyperbolic curve* (example: $AgCOOCH_3$), *or, in parts—by equations of several hyperbolic curves* (example: Ag_2SO_4).

The conclusion just arrived at will not change, of course, if from linear dimensions of the crystals we pass over to their magnitude (G_m) expressed in gram-molecules, and therefore, for the real cases of precipitation, the deduction holds which we have earlier drawn in Section B, that all precipitation curves can be united into either one single universal equilateral hyperbola:

$$G_m \,.\, N = \text{Const.} = K,$$

whence:

$$G_m = \frac{K}{N};^{14}$$

or a straight line:

$$D = a \,.\, N,$$

or, selecting suitable units so as to make a unity—the *median* line:

$$D = N;$$

that is to say, in this latter case, the numerical values of the *"degree of disintegration"* (D) of a precipitate are equal to the numerical values of the *coefficient* N.

It seems useful to subdivide the processes of precipitation into classes and groups, according to the values * of the index m in the *variable* multiplicator:

$$J = k_j \,.\, \left[\frac{Q - L}{L}\right]^m,$$

in the formula of the precipitate form coefficient:

$$N = J \,.\, \frac{Q - L}{L}.$$

The *first class* would, for instance, comprise all cases of precipitation for which: $J = k_j$, *i.e.*: $m = O$. In each group of the first class all cases of precipitation would be centralized, for which: $k_{j1} = k_{j2} = \ldots = k_{jn} = q$, where q is the same number for each group. The *second class* would already be characterized by: $m = 1$, *i.e.*: $J = k_j \,.\, (Q - L)/L$; the principle according to which the cases of precipitation belonging to this class form groups is the same as in the first class. The *third class* would comprise the cases: $J = k_j \,.\, [(Q - L)/L]^2$, and so on.

For studying the precipitation processes with greater exactitude, it would certainly be very interesting to obtain, in addition to the curves with the coördinates: $Q - L_s$ (L_s signifies the *ordinary* solubility of the substance in *pure* solvent) and G_m, also the precipitation curves with the coördinates: $Q - L_w$, G_m and $Q - L_v$, G_m.

On thus substituting the coördinates, simpler precipitation curves must, *in certain cases,* be obtained.

And also, if in the expression: $(Q - L)/L$ we substitute L_w and L_v for L, we may reach, *in certain cases,* a better falling together of the precipitation curves than on substituting L_s.

It is these more exact quantitative investigations of the processes of precipitation of substances that constitute the subject of my own investigations now in hand, as well as of the investigations of my students.

On progressively increasing the concentration of the reacting solutions, cases are also not seldom met with of the appearance, over a definite concentration range, of solid phases that are of quite different chemical composition, such as: hydrates, basic salts, and so on.

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* Under the assumption: $m = m'$ (see above).

In these *complicated* cases of precipitation, the laws deduced above will, of course, also apply to each of such solid phases separately * (*e.g.*, in Fig. 20, which is a purely schematic representation of the case of $SrSO_4$ precipitation from aqueous solutions, the curve $F_1B'C'$ corresponds to the crystals of the unstable hydrate: $SrSO_4 . 2H_2O$, and the curve ABC—to the crystals of $SrSO_4$).

There is one more important consequence which can be derived from the schemes and the drawings of precipitation curves shown in Figs. 4, 6, 9-13, 18, 19. They merely happen to afford *direct* proof that the particles of the so-called "amorphous" precipitates are crystalline.

An examination of the precipitation curves will make it clear to any one who is capable of consequent analytical reasoning, that the compact (not the aggregate) grains of the precipitates which hitherto were described as "amorphous" or "colloidal," represent particles of ultramicroscopic dimensions; and that the crystalline *form* of these particles may, accordingly, not be revealed by optical means.

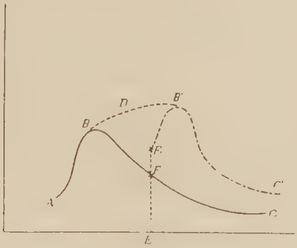

FIG. 20.

But these ultramicroscopic particles do remove † the state of supersaturation of supersaturated solutions, and they are able to grow up until they become microcrystals to be distinctly recognized as such by their very form.

And this latter fact is already *direct* evidence of the crystalline nature of the above ultramicroscopic particles.

The *degree of directness* of this evidence is by no means lesser than that gained by the *Debye-Scherrer-Hull* method of investigating precipitates with X-rays.

This latter method may, however, claim to possess the advantage of a greater demonstrativeness, owing to the "illustrations," the "pictures" it furnishes us with, which are convincing even to those whose power of consequent analytical reasoning is somewhat restricted.

The objection against the "directness" of my method explained above, which was raised by some sceptics and which consists in maintaining that the ultramicroscopic particles of most of the amorphous substances might have undergone, while in state of growth, *conversion* from the amorphous into the crystalline state, is an objection all the more applicable to the *Debye-Scherrer-Hull* method, seeing that the same sceptics may be expected to say about this latter method, that the particles of most amorphous substances are

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* The imaginary circumscribing curve $ABDB'C'$ (Fig. 20)—as well as similar curves drawn for still more complicated cases of precipitation, will also have a maximum, just as real curves have, for corresponding periods of time.

† The rate of this removal is slower, the more the particles are contaminated.

converted into ultramicrocrystals, being exposed to the action of X-rays. I am inclined to regard such criticism as based on a complete misunderstanding with regard to both methods.

D. The Most Important Conclusion to be Derived from the Laws of Precipitation of Substances.

The most important conclusion to be derived from the precipitation laws—and most particularly, from the formula of the precipitate form coefficient:

$$N = J \cdot \frac{Q - L}{L} = J \cdot \frac{P}{L}$$

runs as follows:

Whenever N is extremely large, with every practically attainable value, whether large or small, of $Q - L$ (it being altogether immaterial whether these extremely large values of N had been reached through increasing J or through reducing L), *then every substance, if placed under the above conditions, will practically be present in a typical colloid state, with any practically attainable* $Q - L$.

This conclusion contains no indication whatever within what limits of $Q - L$ the substance will be present in a colloid solution condition, and within what limits of $Q - L$ it will be present under the form of colloid precipitates; because, for a substance, the limiting, maximum concentration of its colloid *solution* also depends on variables as are not represented in the formula for N.

Our conclusion just tells us this much: With every practically attainable $Q - L$ the substance will be present, for some practically sufficient length of time, under either the form of colloid precipitates or the form of a colloid solution; that is to say, for the whole length of this time, it will exist in one of these two forms (colloid solutions, colloid precipitates) of the colloid state.

The problem which confronts us in the synthesis of colloid solutions is preventing the ultramicroscopic crystals, for as much time as possible, from aggregating to non-ultramicroscopic aggregate-flakes, with $Q - L$ as large as possible.

The solution of this problem from the viewpoint of my theory will briefly be given in a later place; what is to be done next, is to discuss, though in rough outlines only, the changes in the chemical composition of the precipitates, dependent on the size of the crystals constituting these precipitates.

IV. THE CHEMICAL COMPOSITION OF PRECIPITATES AS FUNCTION OF THE DIMENSIONS OF THE CRYSTALS COMPOSING THEM. THE FORMATION OF JELLIES

It is a matter of common knowledge that, since *Thomas Graham* and up to our own times, purely chemical interpretations of the colloid state of matter have never been wanting, resulting in the theory of "colloidal, chemically complex compounds" (the various "Complex" theories of colloids), the theory of "gigantic chemical molecules," with the whole variety of its modifications.

My theory of the colloid state is neither "purely chemical," nor is it "purely physical"; it is a "physico-chemical" theory, and therefore it treats phenomena, whenever relevant, from either the physical or the chemical standpoint.

In Fig. 21 crystals are shown of which the size decreases in the sense from right to left.

Suppose we are given one gram-molecule of each sort of crystals, *e.g.*, one gram-molecule of No. 1, . . . , one gram-molecule of No. 10, . . . , one gram-molecule of No. 25, . . . , No. 100, . . . and finally, one gram-molecule of No. *n*.

The hatched portion of the crystals in Fig. 21 is to represent the superficial layer of the crystals, within which the "adsorption" of substances takes place when the precipitates are kept under the solution.

From the standpoint of my theory, it is entirely immaterial what the reasons are which produce adsorption,[15] *i.e.*, whether it be occasioned by the residual chemical affinity, by the tendency of the surface energy to become a minimum, and so on; I shall also abstain here from any attempt to unite under one single principle the whole variety of reasons producing adsorption.

The only thing that matters for my theory is the bald fact that adsorption takes place to some extent at the surface of the crystals.

And this has unequivocally been established by experience.

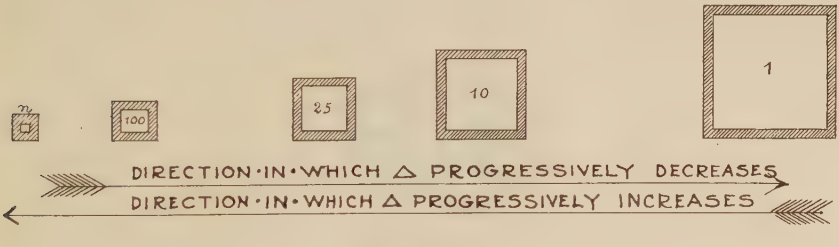
n
100
25
10
1
DIRECTION·IN·WHICH Δ PROGRESSIVELY DECREASES
DIRECTION·IN·WHICH Δ PROGRESSIVELY INCREASES

Fig. 21.

A mere cursory glance at Fig. 21 will make it clear that the smaller the crystal size, the larger is the surface connected with one gram-molecule of the precipitate.

If the crystal No. 1 is sufficiently large, the superficial layer attached to one gram-molecule of the precipitate will be small comparatively, so that the presence of adsorbed matter may not be revealed by analysis of the *usual exactitude*.

Let us designate the substance of the crystal by A and that of the substance adsorbed by B.

In agreement with my theory, the composition of a substance will *always* be expressed by the formula:

$$AB_{\Delta}.$$

Theoretically,[*] as will readily be understood, it is only with crystals infinitely large that $\Delta = 0$, the substance being in a state of absolute purity, *i.e.*:

$$\text{Lim} \,/\, AB_{\Delta} \,/\, \text{with } G_m = \infty = AB_{\Delta = 0} = A.$$

Conversely: if the crystals are of extremely small dimensions ($G_m = \alpha$, where α is an extremely small quantity) Δ will increase very strongly, because (see Fig. 21, crystal No. n) the superficial layer will in this case make up the larger part of the crystals.

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[*] Precipitates as are *practically pure* are certainly obtained with quite finite magnitudes of grain.

It is enough to look at Fig. 21 to understand that, whenever the precipitate grains increase in size while being kept under the solution, there will be a decrease in adsorption, the substance adsorbed being restored to the solvent (*self-purification of precipitates*) by the crystals.

If, on the contrary, the crystals of the precipitate, while under the solution, are progressively crushed, there will be an increase of adsorption.

But, in addition to the separate grains, the precipitates also contain aggregate particles * (see Fig. 22), especially the precipitates made up of very small grains.

From the interstices of such aggregate particles (see black ground in Fig. 22), the mother liquor which is certainly contained therein, is certainly not always easily removed.

This is a circumstance which also affects the chemical composition of the very fine-grained precipitates.

Along with the increase in size of the separate crystals (through either recrystallization or growing together of adjoining crystals) which constitute the aggregate particle, the precipitate is by and by undergoing self-purification.

From what has been just explained it will not be difficult to understand the nature of the changes in composition of the precipitates [16] on the one hand, and of the changes in composition of the solutions these precipitates are contained in, on the other, which take place during the course of the various colloidal processes (*e.g.,* those of aggregation and dispergation).

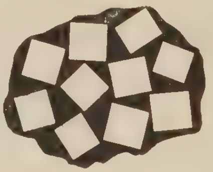

FIG. 22.

In the formula: AB_{Δ} both A and B may of course be elementary as well as chemically composite substances; *e.g.:* $BaSO_4/BaBr_2/_{\Delta}$, $BaSO_4/MnSO_4/_{\Delta}$, and so on; it is also possible, of course, that several substances are adsorbed simultaneously; for such cases we shall have correspondingly: $AB_{\Delta}, C_{\Delta},$ and so on.

The adsorption of other substances by some *definite* substance (*e.g.,* by a $BaSO_4$ precipitate) of some *definite* magnitude of grain, largely depends on the values of the energies with which the truly-dissolved substances are retained by the solvent.

Whenever direct dependence exists of the values of the above energies from the values of the solubilities, *the amount of adsorption bears inverse relation to the solubility of substance adsorbed.*

In Fig. 23 the adsorption curves are given for different salts from aqueous and alcoholic aqueous solutions (the concentration of all salts was almost the same: $= M/100$).

In view of the fact that, for all salts submitted to examination, the solubility diminishes with increasing concentration of alcohol, the curves in Fig. 23 are a thoroughly convincing proof of my above statement.[17]

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* The individual crystals which constitute the aggregate particles may exhibit a vast variety of forms; *e.g.,* they may be fine needles, and so on.

Now that we are speaking of the chemical composition of the various precipitates, we cannot entirely omit jellies.

I discriminate between two kinds of jellies: (1) the *cellular* or *membranous,* and (2) the *continuous network-jellies, i.e.,* such into which the liquid solution gelatinizes with its whole mass (*e.g.,* the gelatination of aqueous gelatin solutions).

Those jellies only may rightly be called *colloidal,* the size of whose constituent crystals belongs to the ultramicroscopic domain.

Cellular jellies are congregations of droplets and streamlets of one of the reacting solutions (*e.g.,* BaI_2) which, being covered by thin membranes of jelly (*e.g.,* $BaSO_4$), are present in the other reacting solution (*e.g.,* $MnSO_4$).

A cellular jelly of that kind can also be prepared, persistent for some time, from gelatin, by pouring a hot aqueous gelatin solution (*e.g.,* at 60° C.) of *suitable* concentration into absolute alcohol which was also heated to a certain constant temperature (*e.g.,* also to 60° C.).

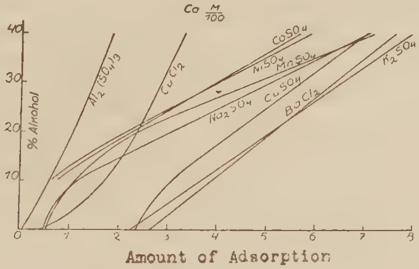

FIG. 23.—Unit of abscissas: 0.01 millimole salt per 1 gram $BaSO_4$.

In this case, owing to the dehydrating action of alcohol, there will be formed, at the surface of the drops of the aqueous gelatin solution, membranes of dehydrated or only partially dehydrated gelatin (this formation occurs practically instantaneously).

In both the above cases of cellular jelly formation the values of

$$N = J \cdot \frac{Q - L}{L}$$

are exceedingly large.

For the formation of continuous network-jellies one additional condition is requisite.[17a]

It is necessary that, with large

$$N = J \cdot \frac{Q - L}{L},$$

the crystallization process should take place, not at the *separate boundary surfaces* (which leads to the formation of cellular or membranous jellies), but *more or less uniformly throughout the whole mass* of the solution.

And to secure this, it is obviously necessary that—in the case of gelatinization being brought about by the addition to any solution, of solutions of some other substance—the solution thus added be able to intermix, without provoking the formation at its surface of non-dispergating (non-dissolving) membranes.

To put it in another way, it is necessary that, during a certain, often very brief, interval after the addition of the substance provoking gelatinization, the system be present in what would be a "supersaturated" (*i.e.*, near the starting) condition, from which it would withdraw by way of crystallization * taking place in a vast number of points of the system, which again takes place with very large

$$N = J \cdot \frac{Q - L}{L}.$$

The mechanism of the formation of continuous network-jellies by cooling the solutions is certainly, in its essence, not a different one from that of the gelatinization of solutions into continuous jellies, at a constant temperature, as provoked by the addition to the solutions capable of gelatinization of solutions of other substances.

In other words, the only difference in the mechanism of formation of membranous and continuous jellies is, that in the latter case there is a sufficiently long "supersaturation period," so that the crystallization might proceed in the whole mass, without provoking the formation of membranes at the boundary surfaces.

It deserves being especially accentuated (in my earlier work I have stressed this on more than one occasion) that there is no difference *in principle, no difference in essence,* so to say—in regard to either the formation mechanism or the structure—between a gelatinous *membrane* of a cellular jelly and a *piece* of continuous network-jelly.

If at all, we may speak here merely of a difference in a purely geometrical sense: in the first case we are facing a gelatinous membrane, *i.e.*, a *planary formation,* with two dimensions (the length and the breadth) predominating over the third (the thickness); in the second case we are confronted with a *spatial gelatinous formation* which coincides in form with that of the vessel in which the solution has gelatinized.

Between jellies prepared under different conditions there exists only a quantitative, not a qualitative difference, *viz.*, in the degree of transparency, the degree of longevity (stability), and the degree of concentration (*i.e.*, of that *minimum concentration* of the substance, at which gelatinization still takes place).†

In due time, I was able to establish that, the greater the solvation capacity of the substance under the *given* conditions, the more insignificant is the concentration of this substance requisite for obtaining a jelly, *other conditions being equal.*

And further: the slower the rate of the desolvation process—the process of solvates rich in molecules of the solvent going over into solvates less rich in such molecules—the longer will the jelly keep without turning into other precipitate forms.

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* Under certain conditions, continuous jellies are formed by coagulation of colloid solutions; in this case it is also necessary that there be a "supersaturation period," and then that the coagulation be more or less uniform throughout the whole mass of the liquid; if this condition is not maintained, it is not continuous jellies, but gelatinous-flaky precipitates that arise. This case either makes certainly no exception to the general rule, as the colloidal solutions of which the coagulation leads to the formation of the jellies could only be obtained with large values of $N = J.\frac{Q - L}{L}$.

† See Bibliography 17a.

Very frequently it occurs that the grainy precipitate obtained as a result of similar desolvations will already occupy by its volume a very small place at the bottom of the vessel, and not the large volume equal to almost the whole capacity of the vessel, which the same substance originally filled while in a solvated condition (under the form of a jelly), having absorbed in the interstices between its crystals the whole of the mother liquor.[18]

Hence the influences become comprehensible exerted by the desolvating factors (both energies and substances) on the decrease in stability of the jellies; with a certain intensity of these factors, there will certainly be no jelly formation at all taking place with the same concentrations as before, but other precipitate forms will arise instead.

It should also be noted (without entering into particulars, not to extend the present paper overmuch) that it would entirely be wrong to separate by an insurmountable barrier, the gelatinous-flaky precipitates from the continuous network-jellies.

Such separation is surely a big mistake, seeing that, in *proper* cases, it is enough *simply* to increase progressively the concentration of the substance provoking the formation of continuous network-jellies, to effect the transition, by very gentle gradations, from gelatinous-flaky precipitates, through weak, precarious network-jellies, to *typical, stable* continuous network-jellies.[19]

As regards the chemical composition of the jellies, their complexity will clearly be understood from their structure.

It is often the case in scientific literature that systems are described as jellies, which consist of microscopic crystals, *e.g.*, of long needles visible with the microscope (this is a property that all substances with so-called [see above] negative crystals have in common) while classing these systems with the colloid formations.

This is quite wrong, because such jellies are already coarsely-disperse, and not colloidally-disperse formations.[20]

V. The Synthesis of Colloid Solutions

A. Solutions of very Small Concentrations.

1. *The Crystallization Method.*—Earlier in the text it was mentioned that in every crystallization the substance goes through a *colloid stage of crystallization.*

The problem of colloid synthesis is to create such conditions, under which this stage would last, not only for seconds and minutes, but for *hours, days, weeks, months, years* and *decades.*

In Fig. 24 the *scheme* is given of a microscopic crystal (sectional view); let the kernel of this crystal *a* be of a size that is beyond the limits of ultramicroscopic vision; kernel *a* + layer *b* will already be of ultramicroscopic dimensions; and the whole crystal (*i.e.*, kernel *a* + layer *b* + layer *c*) will be visible already with the microscope, say—under the most perfect conditions of microscopic vision.

Once a crystal has made its appearance from the solution it has to go through the superultramicroscopic,* the ultramicroscopic, and the microscopic stages of its development.

How are we to fix for a comparatively long time the ultramicroscopic stage of the development of crystals, without allowing them to form aggregate-flakes of microscopic or macroscopic dimensions?

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* I shall not be detained here by an analysis of the process of formation of the smallest of the super-ultramicrocrystals from the molecules (or the atoms).

This question is exactly equivalent to asking: how are we to prepare a comparatively stable colloid solution of a given substance?

The answer is easy, so far as colloid solutions of *very small concentrations* go.

If, for instance, we place the substance under the conditions of negligibly small solubility (see above: Fig. 6), then, even with very small concentrations of the reacting solutions, a large number of ultramicroscopic crystals will be formed, to persist for a comparatively long time.

However, as the concentration of the reacting solutions is very small, the distances between these ultramicrocrystals will not be so very small, and therefore the formation of aggregate-particles will also not be very rapid.

And thus, the colloid stage will last, under the above conditions, for a sufficiently long time for us to notice it.

Here are three examples:

Let us take one liter of ordinary distilled water, and heat it until it boils turbulently; while still boiling, we add * to the water, one after another, 25 c.c. of an aqueous gold salt solution (one gram of $AuCl_3 . HCl . 4H_2O$ in one liter), and 25 c.c. of an aqueous potassium-sodium tartrate solution (14.1 grams of the salt in one liter of water), allowing the mixture to boil for a few minutes more.

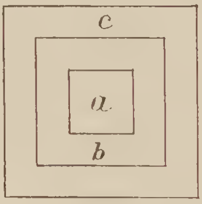

Fig. 24.

After going through a gamut of colors, starting with blue, the final result † will be a colloid gold solution of a wonderful ruby-red color.

Now let us dissolve [21] 0.001 gram of selenium powder in 5 c.c. of aniline, and, with vigorous stirring, pour this quantity into 100 c.c. of ethyl alcohol, which was previously cooled to —80° (or —55°) C.; we shall then obtain a beautiful *yellow* colloid solution of selenium.

The curves in Fig. 25 are those expressing the results of the above colloid synthesis of selenium at different concentrations and different temperatures.[22]

These curves tell us in the most convincing manner that, with increasing $(Q - L)/L$, irrespective of whether this increase is due to the increase of Q or the decrease of L, the dimensions of the selenium particles in the colloid selenium solutions decrease.

And finally, let us pour into 500 c.c. of ethyl ether, previously cooled down to —80° (or —50°) C., with vigorous stirring, 1-5 c.c. of a NaCl solution in methyl alcohol (*e.g.*, a solution containing a few hundredths of a gram of NaCl in 5 c.c.); the result will be a colloid solution of NaCl, with a fine, bluish opalescence.[23]

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* These solutions are better added when also in a boiling condition.

† In the case now under consideration, the tartrate present in excess fulfills one additional function—that of a dispergator (see below).

I could unrestrictedly increase the number of examples, for this is an altogether universal method.

It would be a mistake to believe that it is only by lowering the solubility that the colloid stage of crystallization may be rendered perceptible.

This stage will become fully noticeable if, *e.g.*, the growth of the crystals is very slow, owing to a very slow rate of the dehydration processes which accompany crystallization, and so on.

2. *The Solution Method.*—Earlier in the text it was mentioned that, whenever crystals dissolve, they must go through a *colloid stage of solution.*

Let us place into the solvent, at *relatively* large distances from each other, microscopic crystals of the same kind as those represented in Fig. 24.

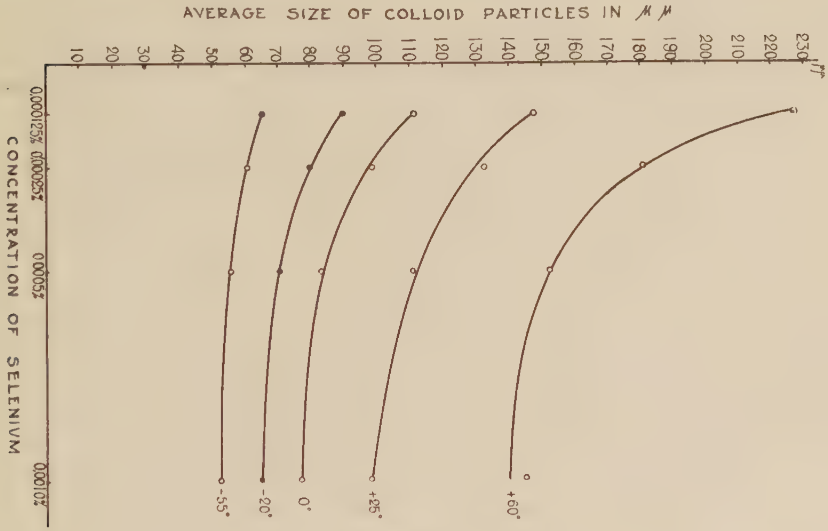

Fig. 25.

It is quite plain that they will begin to dissolve, and that they will become ultramicroscopic—as soon as the layer *c* has dissolved, and superultramicroscopic—when also the layer *b* has dissolved.

Seeing that, with sufficiently large distances between the crystals, these crystals are unable to form aggregate particles at any appreciable rate, it is quite clear that, if the *colloid stage of solution* is to be fixed for intervals of time sufficiently long for its being noticed, it is necessary that the dissolution of the small crystals suspended in the solution be slow.

According to the theory of the solution process of *Nernst-Noyes-Whitney,* the velocity of solution, *other conditions being equal,* is directly proportional to the difference in concentration of the adhering layer and the surrounding solution, and to the diffusion coefficient:

$$V = \frac{D}{\delta} \cdot S(a - x),$$

where $a - x$ is the difference between the concentrations, δ is the thickness of the adhering layer, S is the surface of the crystal undergoing solution, and D is the diffusion coefficient.

From this formula we clearly see that $(a-x)$ must be small, if the colloid stage of solution is to be of long duration; provided, of course, that no other processes whatever, whose progress is slower than that of diffusion, *e.g.*, such as the extremely slowly progressing solvation processes, accompany solution.

It is an easy matter to prepare colloid solutions of *small* concentrations that would persist for periods of time sufficient for observation.

For this purpose, we must first prepare, *e.g.*, by the crystallization method, such precipitates as consist of ultramicrocrystals and aggregates of ultramicrocrystals (in these aggregates, the ultramicrocrystals ought not be solidly grown together).

We next stir up a very small quantity of such a precipitate in a liquid—a liquid which, *when in a state of purity*, will practically not dissolve the precipitate—to which a substance capable of dissolving the precipitate crystals has been added in a suitable concentration.

Thus, a colloid silver precipitate will temporarily go over into a colloid solution, if it is placed in water containing a small quantity of KCN; a colloid tellurium precipitate—in water containing KOH; and finally, a colloid $BaSO_4$ precipitate will temporarily go over into a colloid solution, if introduced into an alcoholic-aqueous medium, to which a proper amount of H_2SO_4 has been added, and so on.

The number of examples is unlimited, for this is an altogether universal method.

For the greatest possible durability of the dispersoid stage of solution with the greatest possible concentration of the ultramicrocrystals, we must certainly avoid the presence in the liquid medium of such substances as would produce an acceleration of the process of aggregate particle formation.

If the concentration of the minute crystals stirred up in the liquid is small, then the relatively large distances separating them from each other will already play the part of a factor attenuating the velocity of aggregate particle formation.

Were this factor missing, the process of dissolution of the crystals would take place in the precipitate at the bottom of the vessel, and not while uniformly (relatively) distributed in the liquid, *i.e.*, not while in a colloid solution condition.

B. Colloid Solutions of Relatively Considerable Concentration.

Under the conditions just described in Section A, colloid solutions of *relatively considerable* concentrations happen to be very unstable, owing to the rapid formation of large aggregate particles, whenever the influences exerted by certain new factors are missing in the system.

The substances or the kinds of energies which produce an increase in stability of the colloid solutions I shall call *dispergators;* * and the substances and energies acting in the opposite sense—*aggregators*.

In this place it should also be noted that, dependent on the conditions (*e.g.*, on the concentration), a *dispergator* may become an *aggregator*, and vice versa.

For the same substance we may have a vast multitude of both *dispergators* and *aggregators*.

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* These are equivalent to *deflocculators* or *protectors*. J. A.

It is an extremely easy matter to find them both.

We must first bring the substance under the conditions of a negligible solubility, and then, by reproducing the formation reaction of this substance, vary the excess of the reacting components of this reaction.

I confine myself to the presentation of four Tables of results obtained for a substance belonging to the "world of crystalloids"—$BaSO_4$, and a substance belonging to the "world of colloids"—aluminium hydroxide.

TABLE I

DISPERGATION OF A $BaSO_4$ PRECIPITATE TO COLLOID SOLUTION

Preparation reaction: $3Ba(C_2H_3O_2)_2 + Al_2(SO_4)_3$—(*in water*).

(In test-tubes about 2 cm. wide.)

To 10 c.c. of a $Ba(C_2H_3O_2)_2$ solution saturated at room temperature, 1 c.c. of a solution of $Al_2(SO_4)_3$ saturated at room temperature was added drop by drop.

After this addition, a coarsely-cellular jelly forms at the surface of the liquid; on slightly shaking the test-tube, the cells sink to the bottom, but soon rise to the surface again.

10 minutes after its formation, the coarsely-cellular jelly was vigorously shaken with the remaining liquid, and a milky-white, barely transparent liquid was thus obtained.

After 9 hours. The clearing of the liquid takes place by zones or layers spreading out in the downward direction; 7 zones may be distinguished: the first zone which is also the clearest, shows a slight bluish-green opalescence; the precipitate zone is at the bottom, and is immediately adjacent to the colloid solution zone, which shows the strongest opalescence and appears yellowish by transmitted light.

After 20 hours. The zones appear somewhat less sharply defined; we have now a 3 cm. layer of a colloid solution—yellow by transmitted light, and showing blue opalescence. The transition zone near the precipitate appears reddish by transmitted light, the red color becoming darker, the nearer to the precipitate.

After 15 days. The colloidally-dispergated precipitate has not yet settled down.

The filtrate is also a colloid solution, yellowish by transmitted light; opalescence—bluish.

TABLE II

An Example of Colloid Synthesis of a Substance Belonging to the "World of Colloids"—Aluminium Hydroxide

The formation reaction was carried out in water.

(In test-tubes about 2 cm. wide.)

To 15 c.c. of aqueous $NH_4(OH)$ solution, 10 c.c. of aqueous $AlCl_3$ solution were added. Concentration: N/40.	To 15 c.c. of aqueous $AlCl_3$ solution, 10 c.c. of aqueous $NH_4(OH)$ solution were added. Concentration: N/40.
A bluish-opalescent liquid forms at once, and almost instantaneously, a translucent, bluish-opalescent precipitate arises in the whole mass of the liquid.	Perfectly clear liquid; barely perceptible opalescence (in a thin body of liquid). *After 2 months.* No appreciable changes.
After 25 minutes from the beginning of the experiment: 4 cm. thick layer of a precipitate in the lower regions of the solution.	*After 8 months.* Very scanty precipitate at the bottom; the liquid shows no marked changes.
After 2 hours and 15 minutes. The precipitate layer has shrunk to 2 cm. The gelatinous-flaky precipitate is somewhat strongly opalescent with a bluish-white shade; the color by transmitted light is of a yellowish shade.	
On being kept standing, the precipitate shrinks down to 1.5 cm., its color becomes a more pronounced white, and it is less transparent. The color by transmitted light is yellow (reddish-yellow).	

TABLE III

AN EXAMPLE OF COLLOID SYNTHESIS OF A SUBSTANCE BELONGING TO THE "WORLD OF CRYSTALLOIDS"—BARIUM SULPHATE

The formation reaction was carried out in 48 per cent alcohol.

(In test-tubes about 2 cm. wide.)

To 15 c.c. of alcoholic-aqueous $CoSO_4$ solution, 10 c.c. of alcoholic-aqueous BaJ_2 solution were added. Concentration: N/40 in 48 per cent C_2H_5OH.

The liquid shows a bluish opalescence; almost immediately, there arise in the whole mass of the liquid very minute particles of a gelatinous precipitate.

After 10 minutes. 1.5 cm. thick layer of gelatinous-flaky precipitate. Small flakes still in suspension. The color of the precipitate is white; the opalescence is greenish-blue. If examined in a test-tube 1.8 cm. in width, the color by transmitted light appears a reddish-yellow (orange).

After 2 hours. The precipitate has shrunk to ¾ of a centimeter. The liquid over the precipitate is somewhat turbid.

After 24 hours. The liquid is clear, everything having settled down.

When investigated with the highest powers of the microscope and with the ultramicroscope, the precipitate was found to consist of extremely small particles and aggregates thereof (flakes); the particles are so small that their shape cannot possibly be established.

To 15 c.c. of alcoholic-aqueous BaJ_2 solution, 10 c.c. of alcoholic-aqueous $CoSO_4$ solution were added. Concentration: N/40 in 48 per cent C_2H_5OH.

The liquid shows a soft bluish opalescence (the color of the liquid is a faint rose, characteristic of the cobalt thiocyanate). Perfectly transparent, so that the filament of an incandescent lamp is distinctly visible through the test-tube with the colloid solution, the light losing almost nothing in intensity. The opalescence slightly increases with time.

After 3 months. No appreciable changes.

Note: A colloid solution prepared by myself under similar conditions as late as in 1907 (by the reaction: $Ba(CNS)_2 + MnSO_4$, in 50 per cent alcohol) has kept up to 1918 stored for 10 years; in the meantime, the opalescence has grown stronger and become less uniform, being weaker in the upper layers; a very small precipitate has formed at the bottom.

TABLE IV

INFLUENCE EXERTED BY THE INCREASE IN CONCENTRATION OF THE BaI_2 SOLUTION ON THE DISPERGATION PROCESS OF A $BaSO_4$ PRECIPITATE IN AN ALCOHOLIC-AQUEOUS MEDIUM (47.5 PER CENT ETHYL ALCOHOL)

Procedure adopted for the experiments: To 11 c.c. of a $CoSO_4$ solution of N/40 concentration in 47.5 per cent alcohol, 10 c.c. of a BaI_2 solution of the same N/40 concentration and in the same medium were added. The mother liquor was then poured off, as carefully as possible, from the gelatinous-flaky $BaSO_4$ precipitate. The fresh precipitates of $BaSO_4$ thus obtained, which were all prepared in exactly the same way (the volume occupied by the precipitate together with the remaining mother liquor amounting to about 2.5 c.c.), received each an addition of 10 c.c. of alcoholic-aqueous (47.5 per cent) BaI_2 solution of the following progressively decreasing concentrations: 2N, N, N/4, N/12, N/24, N/40, N/80, N/200 and N/400. The systems obtained by shaking these mixtures for a short while (they are correspondingly designated as: D_1, D_2, D_3, D_4, D_5, D_6, D_7, D_8, and D_9) were then submitted to observation and comparison.

D_1. The precipitate has dispergated into a turbid though translucent liquid; on slightly shaking the liquid, one may clearly perceive the streaks of precipitate * to appear in the liquid. *After 28 minutes:* the precipitate has partially settled down, and partially remains in suspension. *After 42 minutes:* almost the whole of the precipitate is already at the bottom forming a layer about 1 cm. in height (the experiments were carried out in test-tubes about 1.8 cm. in diameter); isolated flakes are still in suspension. *After 24 hours:* the liquid over the precipitate is quite clear.

D_2. The precipitate has dispergated into a turbid though translucent liquid, which displays distinct streaks of precipitate on being shaken. *After 25 minutes:* small flakes in the whole body of the liquid. *After 40 minutes:* an 8 mm. thick precipitate layer has formed; the remaining flakes still in suspension. *After 24 hours:* the liquid over the precipitate is perfectly clear.

D_3. The precipitate has dispergated into a liquid more transparent than is D_2. *After 18 minutes:* well pronounced streaks due to the particles present in the liquid; but there is no formation of flakes, as was the case in D_2. *After 33 minutes:* turbid, somewhat translucent liquid; streaks on shaking. *After 3 hours and 30 minutes:* a precipitate coating at the bottom; over the precipitate—a turbid liquid with particles suspended therein. *After 24 hours:* the precipitate coating has become greater; over the precipitate—a somewhat turbid liquid, displaying streaks. *After 72 hours:* the liquid is less turbid, the precipitate has increased. *After 10 days* (ten times 24 hours): the precipitate (fine-grained flakes) has settled down; the liquid over the precipitate is still somewhat turbid.

D_4. The precipitate has yielded, by dispergation, a colloid solution showing strong bluish-white opalescence and appearing yellowish by transmitted light. *After 3 days:* a fine, discontinuous precipitate coating (by microscopic examination (Apochr. 16 mm.; Okul. 18) this precipitate coating proved to consist of dust particles covered with precipitate, and also of larger particles); over the precipitate—a beautifully opalescent, and well translucent colloid solution. *After 10 days:* no important changes.

D_5. The precipitate has yielded, by dispergation, a colloid solution displaying a still finer opalescence, and still more translucent than that in D_4. *After 3 days:* precipitate coating, though smaller than in D_4. (The results obtained by microscopic investigation were the same as in D_4.) The colloid solution over the precipitate is less strongly opalescent and more transparent than in D_4. *After 10 days:* no important changes.

D_6. The precipitate has yielded, by dispergation, a colloid solution somewhat more opalescent than that of D_5. *After 3 days:* the precipitate coating is somewhat larger than in D_5. (The results of microscopic examination—the same as in D_4 and D_5). The colloid solution over the precipitate is more strongly opalescent than in D_5. *After 10 days:* no important changes.

D_7. The precipitate has yielded, by dispergation, a colloid solution almost identical with that of D_6. *After 3 days:* nearly the same as in D_6; the opalescence of the solution is, however, somewhat stronger than in D_6. *After 10 days:* no important changes.

D_8. The precipitate has yielded, by dispergation, a colloid solution of which the opalescence is somewhat stronger than that of D_7. *After 3 days:* precipitate coating similar to that in D_7. The colloid solution over the precipitate is more strongly opalescent than D_7. *After 10 days:* no important changes.

D_9. The precipitate has dispergated into a liquid which displays strong (whitish) opalescence and distinct streaks of precipitate; the liquid is more turbid, of course, than were D_8, D_7 and D_6, and beyond comparison more turbid than were D_5 and D_4; it is about as turbid as D_3. *After 10 minutes:* the streaks have become more distinct, but they are still weaker than in D_3. *After 3 days:* the precipitate coating is greater than in D_8, D_7, D_6, D_5 and D_4, but smaller than in D_3. The colloid solution over the precipitate is strongly opalescent with a bluish-white tinge, and fairly well translucent with a yellowish colour; the precipitate coating appears also yellowish by transmitted light. *After 10 days:* near the surface the liquid has become quite clear (the particles have sunk quite 4 mm. from the surface); the other parts of the liquid are still a colloid solution (approaching a suspension) which shows strong opalescence; precipitate coating at the bottom.

A comparison of the systems with each other 10 days (10 times 24 hours) after their preparation.

D_1 and D_2 —precipitates at the bottom; over the precipitates—a transparent liquid.

D_3 —the greater part of the suspended particles have settled down as precipitate; the liquid over the precipitate is somewhat turbid.

D_4, D_5, D_6, D_7 and D_8—the $BaSO_4$, except for a trifling part (the precipitate coating, also the effect of dust), is present in a colloid solution condition. *The concentration corresponding to the dispergation maximum* lies somewhere near D_5.

D_9 —a system approaching the suspensions. Precipitate coating at the bottom.

Investigation of the filtrates obtained from D_1 and D_2 after diluting them with water.

To 6 c.c. of water, 3 c.c. of the perfectly clear filtrates of D_1 and D_2 (the filtration was effected through No. 590 "Schleicher & Schuell" double filters) were added correspondingly. In both cases, a distinct turbidity was observed to appear in the liquids after 10-15 minutes, being stronger in D_1 than in D_2, which proves that the solubility of the $BaSO_4$ has increased at the expense of the *complex compounds* to a somewhat greater extent in D_1 than in D_2.

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* On shaking a liquid containing in suspension such particles as are invisible, on account of their minuteness, with the naked eye, but can be descried with a magnifying glass (of tenfold magnification), we observe a peculiar movement to take place in the stirred up layers of the liquid; this phenomenon is designated as "streaks of precipitate." (It appears in V_2O_5 sols. J. A.)

From the contents of these tables it becomes clear that, as in the case of the aluminium hydroxide, aluminium salts fulfil the part of *dispergators,* and ammonia—that of an *aggregator,* just the same in the case of $BaSO_4$, it is *barium salts* that act as *dispergators,* and the $MnSO_4$ (and other sulphates)—as *aggregators.*[*]

As we see from Table IV dealing with the experiments on dispergating a $BaSO_4$ precipitate, at a certain concentration the *dispergator* becomes an *aggregator.*

In Fig. 26 and Fig. 27 the stability[†] (duration of life) curves are given of colloid $BaSO_4$ solutions in alcoholic-aqueous media (about 63 per cent alcohol), dependent on the excess concentration of the barium salt solution (in the present case—of $BaCl_2$ and $Ba[NO_3]_2$).

It is clear from these curves that, above a certain concentration, the *dispergator* turns into an *aggregator.*

We thus come to see that the stability of a colloid solution decreases as the concentration of $BaSO_4$ increases (at a certain, sufficiently considerable, concentration of $BaSO_4$ colloid solutions are able to persist only for a few minutes), as well as beginning with a certain concentration of the *dispergator.*

The Figs. 26 and 27 will also help us to understand the so-called "washing-method" of precipitates applied for converting them into colloid solutions again.

For, reducing the concentrations, *e.g.,* of the barium salts present in the $BaSO_4$, by washing these precipitates with alcoholic-aqueous medium, makes the barium salts become dispergators again.

But if the colloid precipitate of $BaSO_4$, with barium salts adsorbed therein, is mixed together with a *sufficiently large* amount of a mixture of alcohol and water, then the concentration of the dispergator will be lowered to such an extent that the colloid solution will become very unstable.[‡] (See Figs. 26 and 27.)

An attentive examination (Figs. 26 and 27) of the dispergation[§] curves will also disclose that, under *suitable* conditions, the *dilution* of a colloid solution with the pure dispersion medium makes its life shorter and produces an acceleration in the coagulation process.

These facts, which unfortunately have as yet not been sufficiently well understood, afford evidence that it is precisely *the changes in the course of the dynamic (kinetic) processes taking place at the surfaces of the particles in the colloid solutions, that are the reasons producing coagulation, and that the changes in the electric conditions on the above surfaces are but consequences of the reasons just named.*

As to the nature of the mechanism of dispergation, it can briefly be explained as follows:

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[*] Under different conditions of precipitation, the ammonia (for the aluminium hydroxide) and the sulphates (for $BaSO_4$) may become *dispergators.*

[†] For a more detailed account, see P. P. von Weimarn, K. Aoki and S. Kataoka, "Some Quantitative Contributions to P. P. von Weimarn's Theory of Dispergation," now being prepared for *Kolloid-Chem. Beihefte.* (The dispergation curves have also been studied with $BaBr_2$ and BaI_2.) The dispergation curves (see Figs. 26 and 27) are always of the same general form (*i.e.,* they have maxima), *if only the condition holds that the values of* $(Q - L)/L$ *be sufficiently high.* My theory of dispergation was explained for the first time in my communication delivered before the Russ. Chem. Soc. on Dec. 17 (4), 1908: "The Parallelism between Peptisation and Solution," *Journ. Russ. Chem. Soc.,* 40, 1785 (1908). Compare also: *Koll. Zeit.,* 4, 123 (1909); *Kolloidchem. Beih.,* 1, 399 (1910); "Grundzuege der Dispersoidchemie," 73 and following (1911); "Kolloides und kristalloides Loesen und Niederschlagen," 541-638, Kyoto, 1921.

[‡] It is very important to understand this, for dealing consciously with colloid synthesis.

[§] As in due time it has been pointed out in my papers (*loc. cit.*) devoted to my theory of dispergation, similar sets of dispergation curves can be obtained for every substance (elementary substances, oxides, salts and so on).

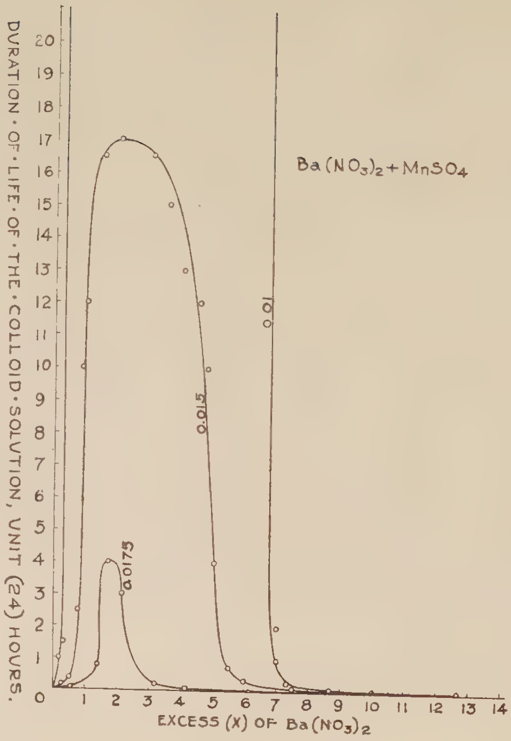

FIG. 26.

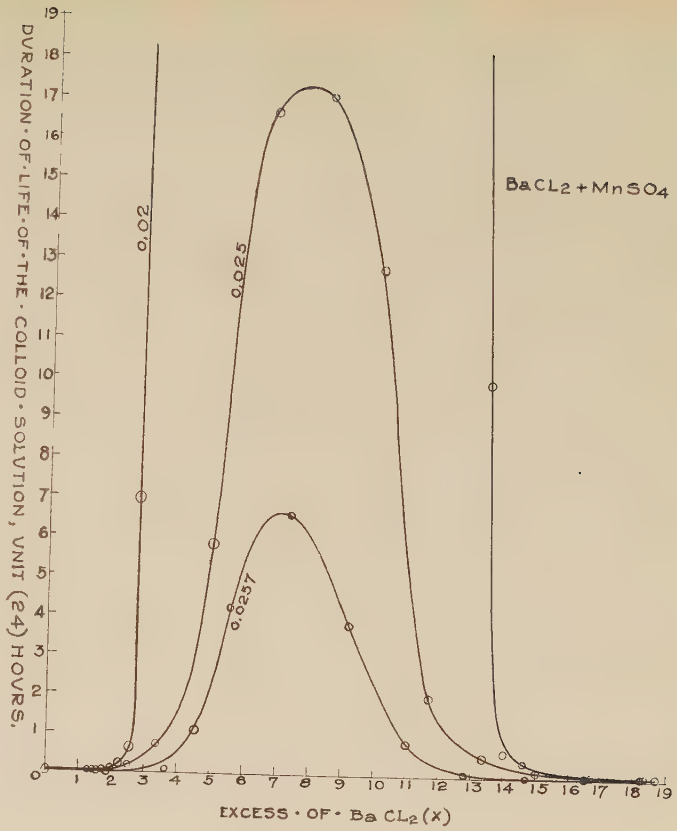

FIG. 27.

Into 50 c.c. of a solution of Ba(NO$_3$)$_2$ (or of BaCl$_2$) in 63% ethyl alcohol of the concentration (in gram-equiv., *i.e.*, normal) '$a + x$', 50 c.c. were poured, of a MnSO$_4$ solution in 63% ethyl alcohol of the concentration 'a'. The abscissas are the values for 'x', the unit being = 0.001 normal concentration. The values of concentration 'a' are given in the curves.

The atoms or the groups of atoms which constitute the molecules of an either truly or solutoidally (see later) soluble dispergator, mutually interact with the atoms or the groups of atoms of the *superficial layer* of the ultramicrocrystals.

Consequent on this interaction, a definite number of molecules of the dispergator will be present, at any given moment, at the surfaces of the ultramicrocrystals; it is at the expense of these molecules of the dispergator that the ultramicrocrystals parasitize and keep suspended within the colloid solution.

And it is for this reason that, in due time,[24] I bestowed on the dispergation phenomena the name of *dispersoidal parasitism* phenomena.

The *dispersoidal parasitism* is a *dynamic* (kinetic), and not a static process; it is very important that this should be well understood.

If dispergation is to be a success, the intensity of atomic interaction between the molecules of the dispergator and those of the superficial layer of the ultramicrocrystals must not exceed a definite limit.

With higher, as well as with lower values than those corresponding to this limit, the stability of the colloid solution becomes lower.[25]

With sufficiently high intensity of the above atomic interaction there takes place the formation of a chemical compound of molecules of the dispergator and molecules of the ultramicrocrystals (so, for the case of the barium salts acting as dispergators, $BaSO_4$ being the substance undergoing dispergation, there will form complex salts of the general type: $aBaSO_4 . bBaX_2 . cH_2O$).

Such substances may also be dispergators as have no atoms or atomic groups in common with the substance undergoing dispergation; for instance, such chemical substances as are truly or solutoidally soluble in the given liquid medium, and whose composition includes such atoms as would exhibit, when in a free state, strong activity toward certain atoms of the substance undergoing dispergation.

The general equation regulating the duration of the existence of colloid solutions will be the following: [26]

$$G_A - G_D = \pm \Delta,$$

where: G_A is the velocity of aggregation, and G_D the velocity of dispergation.

For a greater length of life of colloid solution, it is necessary that the absolute value of Δ be very small.

When $\Delta = O$, we have the case of permanent stability.

In the theoretical part of the present paper it was pointed out that, under certain conditions, such colloid solutions can be prepared for every substance, as contain an equal (average) number of crystals in unit volume.

The above quoted tables with the data pertaining to colloid synthesis of the aluminium hydroxide and the $BaSO_4$ make the possibility comprehensible of a real approximation of the above theoretic deduction.

VI. The Solutoids

The particles of any substance whatever which are present in a liquid medium may have colloid (ultramicroscopic) dimensions not merely as a result of fixation, for a more or less considerable length of time, of either the *colloid stages of solution* ($-\Delta$, very small) or those of *crystallization* ($+\Delta$, very small), but also as the result of other reasons, in the presence of which Δ is already equal to zero, *as with true solutions* (permanent stability).

In due time I have called this species of the colloid state the *solutoid* species, because this state is actually most like the state of a true solution.

On the other hand, for substances present in a solutoid condition, it is especially easy to fix, for relatively lasting periods of time, the *colloid stages* of both solution and crystallization.

There are several reasons which may produce the *solutoid* state.

In the first instance, the diameter of the molecules of certain substances (*in a desolvated condition*) may reach colloidal dimensions if these molecules are complex, *i.e.*, if they contain a *large number* of atoms of different elementary substances; *e.g.*, proteins and other chemically complex substances.

Further, there are substances which, by virtue of their chemical nature (*irrespective of the nature of the solvent*), are capable of polymerization and association; through this polymerization and association such polymeric molecules may arise which already have colloid dimensions.

Thus far, we have only considered the complex or the polymeric substances when in a desolvated condition, and, in general, independently of the nature of the solvent.

Taking this latter into consideration, it might be expected that, by strongly reducing the dielectric constant of the medium, it would become easy to convert into the *solutoid* state whatever substance desired, *i.e.*, into the state of a solution with gigantic molecular associations of the substance contained therein.

Experience shows, however, that the majority of substances usually dealt with * are *practically* insoluble in media with small dielectric constant, *i.e.*, in other words, if ever the *solutoid* state is realized in solvents of that kind, it is only in *vanishingly* small concentration.

But there exists a reason of *universal* character which can actually effect the conversion into the solutoid state of any substance, even of a substance which, when in a desolvated condition, is chemically quite simple (*e.g.*, the NaCl).

This reason is solvation, and the association of solvated molecules connected with this solvation.

Gigantic solvated molecules (giant-solvated-molecules) *can, in principle, be obtained for every substance, and it is precisely in this sense that I asserted that the solutoid is also a universal state of matter.*

This principle, making part of my theory of the colloid state of matter, admits being easily demonstrated experimentally by means of numerous examples.

It is enough to look at the tables of solubilities of solid substances in liquids, to understand that an ample solubility of these substances is in some way connected with the solvation processes, and that at low temperatures, crystals-solvates are obtained with larger amounts of molecules of the solvent.

Hence it is clear that, through rapidly transferring the solutions to low temperatures, the fixation of solvates with larger quantities of molecules of the solvent is possible.

If we remember that the molecular weight of $30H_2O$ amounts to 540.48, we shall easily understand that it is by no means difficult to obtain, at low temperatures, such associations of hydrate molecules whose total molecular weight amounts to several thousands.

It is also easy to understand that the velocity of conversion of hydrated molecules of different grades of hydration into those of the hydrate most stable under the given conditions is small at sufficiently low temperatures.

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* It is self-evident that, in solvents of the above type, those solid substances are well soluble which are chemically active toward them.

If we take into consideration these two circumstances, it will become clear to us that, exactly the same physico-chemical conditions arise for any substance at low temperatures, if this substance is present in a solvent in which it is strongly solvated, as those which naturally exist for the aqueous solutions, *e.g.*, of gelatin and agar, over the range of ordinary temperatures (between 100° and 0° C.).

The velocity of conversion of the hydrated gelatin (or agar) molecules of different degrees of hydration into those of the hydrate which is the most stable under the given conditions, is already small within the ordinary temperature range.

It thus occurs that, within a certain domain of *low* temperatures the solutions of substances in solvents in which they are strongly solvated, will be present in a typical solutoid state, quite similar to the same state of gelatin and agar in their aqueous solutions at ordinary temperatures.[27]

During crystallization * of solutions of substances present in solutoid condition, we shall witness the process of reversible gelatinization; for, in the cases under consideration,

$$N = J \,.\, \frac{Q - L}{L}$$

is large even with comparatively small values of $(Q - L)/L$, being enormous with the medium and the large values of $(Q - L)/L$; in these cases, J is very large.

And so, with a *sufficiently rapid* † cooling of solutions—of the type now under discussion—of substances, there will arise jellies or *quite solid* jellies (glasses) which, on being *sufficiently rapidly* heated, will undergo reversible conversion into the original solutions, while no microscopically visible particles are separated out.

Alcohol-water mixtures, as they permit being cooled down to very low temperatures without the solvent crystallizing out, are especially convenient for the preparation of such reversible jellies.

Two tables with experimental data will lend convincing confirmation to all that has been said above.[28]

And thus, *the gelatinization process of solutoid solutions is a crystallization process, and the jelly consists of ultramicrocrystals ‡ or, more generally* (so as to include also the *extremely high* degrees of dispersity), of *vectorial ultramicroparticles of various solvate forms.*

Quite similarly, we may arrive at the conclusion that the glasses of also the so-called unitary (einheitlich) substances represent accumulations of numberless multitudes of vectorial ultramicroparticles, these ultramicroparticles belonging, in many cases, to different modifications of particles of the given substance.§

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* In the present connection, it should be noted that, for the substances of high molecular weight, the *gram-molecular* solubilities are small, even when their percentage solubilities are comparatively large. For instance, for substances of the molecular weight 10.000, a one per cent solution is but a solution of 1/1000 gram-molecular concentration. Not infrequently, the *relatively* good solubility of the solutoids is only an apparent one, being due to the fact that the solventolysis products of these solutoids are better soluble, and to the fact that, to a certain extent, these products act as dispergators for the molecules, as yet unsolventolized, of the solutoid.

† On cooling slowly, water of the hydrated molecules, the feebly bound, at higher temperatures is easily squeezed out in crystallization, even if the hydration is very great.

‡ The ultramicrocrystals may exhibit various forms; they are needles in the case of negative crystals.

§ In the literature the name of Naegeli is often associated with the hypothesis if the crystalline nature of amorphous and colloid substances; historically this is quite wrong; the origin of this hypothesis dates back to much earlier times than when Naegeli wrote; this hypothesis should most correctly be associated with the name of M. L. Frankenheim, though it was not created by him;

TABLE V

(The aqueous solutions of the salts enumerated below applied for the experiments were nearly saturated at room temperature.)

Designation of the Substance	Solubilities and Hydrate Forms	Behavior on Being Rapidly Cooled in Liquid Air
1. $Mn(CNS)_2$.	Solubility at 20° C. of the salt with four molecules hydrate water—135 gr. anhydrous salt in 100 gr. water. *Hydrates:* $2H_2O$, $3H_2O$ and $4H_2O$.	Perfectly transparent solid jelly (glass) of light-green color. The original color of the solution was dark-green.
2. $Sr(CNS)_2$. 3. $Ca(CNS)_2$. 4. $Ba(CNS)_2$.	Solubilities and hydration ability—nearly the same as for the $Mn(CNS)_2$.	Colorless solid jelly (glass), clear as water.
5. $Al_2(SO_4)_3$.	Solubility at 20° C. of the salt with 18 molecules hydrate water—36 gr. anhydrous salt in 100 gr. water. *Hydrates:* $10H_2O$, $18H_2O$, $27H_2O$—at low temperatures.	Do.
6. $CaCl_2$.	Solubility at 20° C. of the salt with 6 molecules hydrate water—74 gr. anhydrous salt in 100 gr. water; solubility at —25° C.—50 gr. anhydrous salt in 100 gr. water. *Hydrates:* $6H_2O$, $4H_2O$, $3H_2O$, $2H_2O$, H_2O. According to some indications—also $15H_2O$ (*de Coppet*):	Do.
7. Fe_2Cl_6.	Solubility at 20° C. of the salt with 12 molecules hydrate water—92 gr. anhydrous salt, at —27° C.—54 gr. anhydrous salt in 100 gr. water. *Hydrates:* $12H_2O$, $7H_2O$, $5H_2O$, $4H_2O$.	At first—transparent solid jelly (glass) of yellow color; then—rapid change in color into light-green.
8. Li_2CrO_4.	Solubility at 18° C. of the salt with 2 molecules hydrate water—111 gr. anhydrous salt in 100 gr. water. There are no indications in literature that other hydrates should exist.	Yellow, transparent solid jelly (glass) which does not change in color.
9. $Na_4Mn(CNS)_6.12H_2O$. 10. $K_4Mn(CNS)_6.xH_2O$.	Very readily soluble salts, and very capable of hydration.	Jellies and glasses form easily.

Note: In addition to the substances enumerated in the above table, the formation of altogether transparent solid jellies, on rapidly cooling concentrated aqueous solutions (*at a suitable concentration*), can also successfully be demonstrated under application of the following substances: H_2SO_4, $MnSO_4$, $ZnCl_2$, $Pb(ClO_3)_2$, $ZnBr_2$, $Al(NO_3)_2$, ZnI_2, $KHCO_2$, potassium arsenite, NaCNS, and, of course, of other compounds showing inclination toward solvation, and well soluble in water.

TABLE VI

Solidification of Alcoholic-aqueous Salt Solutions when Placed in Liquid Air

(The alcoholic-aqueous solutions of the salts enumerated below applied for the experiments were nearly saturated at room temperature.)

Designation of the Alcoholic-aqueous Salt Solution	In 10 mm. Wide Test-tubes	In 1-3 mm. Wide Test-tubes
NaCl I.	Perfectly transparent solid jelly (glass).	Do.
NaCl II.	Do.	Do.
NaCl III.	Do.	Do.
NaCl IV.	The outer parts of the solid jelly show bluish opalescence; the inner parts appear white by incident, and reddish by transmitted light. (The appearance of both opalescence and turbidity is due to the fact that, as has been shown by special experiments, it is water, and not NaCl, that is separated out.) On heating, a liquid results, clear as water, which begins gradually to separate out NaCl crystals on further heating.	Perfectly transparent solid jelly (glass).
KCl I, KCl II, KCl III, $CaBr_2$ II, CaI_2 II, Rb_2CO_3 I, Cs_2CO_3 I, NaI I, NaJ II, NaJ III, KBr I, KBr II, KBr III, $AgNo_3$ I, $AgNO_3$ II, $AgNO_3$ III, KI I, KI II, KI III, RbBr II, NaBr I, NaBr II, NaBr III, NaBr IV, RbCl I, NaCNS I, NaCNS II, NaCNS III, NaCNS IV, NaCNS V, NaCNS VI, KCNS I, KCNS II, KCNS III, KCNS V, KCNS VI, NH_4CNS I, NH_4CNS II, NH_4CNS III, NH_4NO_3 I, NH_4NO_3 II, NH_4NO_3 III, NH_4Cl I, NH_4Cl II, NH_4Cl III.	Solid jellies (glasses), clear as water; on being relatively *slowly* heated, they turn turbid, owing to the coarsely-dispersed phase which has separated out.	In narrow test-tubes there will certainly also arise solid jellies clear as water; these, however, on being *rapidly* heated, revert in many cases to the original solution again, without separation of coarsely-dispersed phases intermediately.

Note: The Roman numerals: I-VI appended to the salt formulas are to indicate the following concentrations of ethyl alcohol correspondingly: 99.4 per cent, 99 per cent, 92.27 per cent, 85.6 per cent, 83.1 per cent and 76.83 per cent. The abbreviated designations in the table, as *e.g.:* NaCl I, NaCNS II, KCl III, NaCl IV, NaCNS V, KCNS VI, thus signify correspondingly: sodium chloride solution in 99.4 per cent alcohol, saturated at room temperature; sodium thiocyanate solution in 99 per cent alcohol, saturated at room temperature; potassium chloride solution in 92.27 per cent alcohol, saturated at room temperature; sodium chloride solution in 85.6 per cent alcohol, saturated at room temperature; sodium thiocyanate solution in 83.1 per cent alcohol, saturated at room temperature; potassium thiocyanate solution in 76.83 per cent alcohol, saturated at room temperature; and so on. Here "saturated" means *almost* saturated.

In concluding the present paper, I feel myself called upon to point out with much emphasis that, conformedly to its extent, I was able to give only the main foundations of my theory of the colloid state, and that certain parts of my theory had to be entirely omitted,[*] or could be given but very brief consideration.

I believed it to be important to dwell, at the greatest possible length, on the process of precipitation; because, as soon as we are able to arrive at such conditions for the substance, that its precipitation curve lies, with its largest part, within the ultramicroscopic domain, this means as much as solving the very outstanding problem of colloid synthesis.

To convert a colloid precipitate into a colloid solution is already easy: it is the reaction components (often but one of them, under usual conditions), that in the first place may serve as dispergators; and in the second place — the substances which, being either truly or solutoidally soluble in the given liquid, show but feeble atomic interaction with the substance undergoing dispergation [†] (*e.g.*, certain chemically composite substances, of which the composition includes *such atoms of elementary chemical substances as are especially active when in a free state*).

But the precipitation process is certainly not the only means available for obtaining precipitates suitable for being dispergated to colloid solutions.

There exists another general method.

This method could certainly be only suggested by him who was *thoroughly* convinced that "Crystal" and "Colloid" are not antithetic concepts, are not two separate "worlds of matter."

I am speaking of my mechanical method of colloid synthesis which I proposed in 1910.[§]

The results obtained by this method (*N. Pihlblad, A. L. Stein, S. Utzino*) are communicated in the present volume by my student *Mr. S. Utzino.*

I can only say that the results obtained thoroughly coincide with the requirement of the law established by myself—the law of the universality of the colloid state of matter.

Even though the electric dispersion of substances (the *Bredig-Svedberg* method) could yet be interpreted by some investigators as a process of conversion of a crystalline substance into a *special colloid* or a *special colloidally-amorphous* condition, this interpretation may hardly be logically applied at all, to my mechanical synthesis of colloid precipitate and colloid solutions.[‡]

And therefore, the very fact of preparation, by this latter method, of substances in a colloid condition, is also a *direct* proof of the correctness of my theory of the crystalline nature of amorphous and colloidal precipitates.

The readers who might wish to acquaint themselves in more detail with my theory of the colloid state of matter, are referred to my following works:

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see historical part of my book, "Kolloides und kristalloides Loesen und Niederschlagen," Kyoto, 1921, pp. 277 and following.

[*] For instance, I had to leave out that part of my theory which deals with the electric properties of the colloids. I only wish it to be pointed out here that I am categorically opposed to any overestimation of the rôle fulfilled by the electric energy in all natural phenomena in general. Concerning the rôle it fulfils in the stability of colloid solutions, we should not forget that other kinds of energies, *e.g.*, centrifugal force (*i.e.*, highly strengthened gravitation energy), are equally able to annihilate stability, just as is the electric energy (electrophoresis).

[†] A more detailed account of my dispergation theory was given in my earlier articles (*loc. cit.*).

[§] Cf. p. p. von Weimarn, *Kolloid Z.*, 37, 151 (1925); P. P. von Weimarn and S. Utzino, *ibid.*, **36**, 265 (1925).

[‡] It should be noted, however, that conversion from one crystalline form into another, weakening of the union with water in the hydrates, dehydration, even fusion processes (as well as chemical reactions), are quite possible, whenever a high degree of dispersity was reached by the mechanical method; see P. P. von Weimarn, *Koll. Zeit.*, 12, 125 (1913). On the weakening of the union with water in hydrates with crystallization water, a communication is made in the present volume by my student, Mr. T. Hagiwara.

I. "Zur Lehre von den Zustaenden der Materie." 1914.[29] Verlag von *Theodor Steinkopff*, Dresden.
II. "Grundzuege der Dispersoidchemie." 1911. Verlag von *Theodor Steinkopff*, Dresden.
III. "Kolloides und kristalloides Loesen und Niederschlagen." Kyoto, 1921. By now sold out. (The second edition has appeared, in 1925, Verlag von *Theodor Steinkopff*, Dresden.)

Nov., 1925,
Osaka, Japan.*

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1. W. Nernst, "Theoretical Chemistry," English Ed., p. 638, 1911.

2. W. Nernst, *Ibid.*, p. 586. Concerning the inconsistency of the objections raised against this theory, see my book: "Kolloides und kristalloides Loesen und Niederschlagen," Kyoto, pp. 480-490, 1921.

3. Concerning the preparation conditions of these precipitates, see: "Zur Lehre von den Zustaenden der Materie," zwei Baende; Verlag von Theodor Steinkopff, Dresden, 1914. The microphotographs in Plate I correspond to the following figures in Bd. II (Atlas) of the above-named book: No. 1—Fig. 100; No. 2—Fig. 50; No. 3—Fig. 39; No. 4—Fig. 26; No. 5—Fig. 92; No. 6—Fig. 94; No. 7—Fig. 96, and No. 8—Fig. 99.

4. See: A. E. H. Tutton, "Crystallography and Practical Crystal Measurement." Macmillan & Co., London, 1911, p. 539.

5. Compare: P. P. von Weimarn, "Grundzuege der Dispersoidchemie," 50-51 (1911). Verlag von Theodor Steinkopff, Dresden.

6. Compare, *e.g.*, P. P. von Weimarn, "Four Laws on the Mutual Influence of Salts on their Solubility." *Koll. Zeitschr.*, 32, 145-150 (1923).

7. P. P. von Weimarn, "On the Influence of the Concentration of the Reacting Solutions on the Form and the Structure of Precipitates when the Reactions are Realized in Presence of Agar or Gelatin." *Jour. Russ. Chem. Soc.*, **44**, 728 (1909); Abstracts: *Koll. Zeitschr.*, 6, 180 (1910). On the influence exerted by molecules of foreign substances on the dimensions of the individual crystals, s. P. P. von Weimarn, *Kolloidchem. Beih.*, 4, 77 (1912). Compare: On the influence of gelatin on the structure of silver halide precipitates, in the book by A. P. H. Trivelli and S. E. Sheppard; "The Silver Bromide Grain of Photographic Emulsions," 35-39 (Fig. 10-12), 1921. Eastman Kodak Company, Rochester, N. Y. It should be noted, however, that, throughout the works of these authors, no strict distinctions have been observed between the *individual* and the *aggregated* (i.e., representing aggregates of the former ones) particles.

8. The precipitation processes of Ag_2SO_4 from aqueous and alcoholic-aqueous solutions were studied, under my direction, by my student Mr. S. Otsuka, in 1922, in the laboratory of physical chemistry of the Kyoto Imperial University (Director: Prof. Dr. Y. Osaka); see: P. P. von Weimarn, *Koll. Zeitschr.*, 33, 232-237 (1923); for more details, see: P. P. von Weimarn and S. Otsuka, "The Precipitation Laws as Instanced by the Precipitation of Ag_2SO_4 from aqueous and alcoholic-aqueous solutions," now in state of preparation for the *Kolloidchem. Beih.*; s. Reference No. XXV.

9. The precipitation processes of silver acetate from aqueous and alcoholic aqueous solutions were studied, under my direction, by my student, Mr. H. Hori, in 1923, in the laboratory of physical chemistry of the Kyoto Imperial University (Director: Prof. Dr. Y. Osaka); for a more detailed account, see: P. P. von Weimarn and H. Hori, "The Precipitation Laws as Instanced by the Precipitation of Silver Acetate from Aqueous and Alcoholic-Aqueous Solutions," now in state of preparation for the *Kolloidchem. Beih.*; s. Reference No. XXV.

10. See: P. P. von Weimarn, "Grundzuege der Dispersoidchemie," pp 27 and following (1911). Verlag von Theodor Steinkopff, Dresden.

11. It is interesting to note (for particulars, see: P. P. von Weimarn and S. Morishima, "The Precipitation Laws as Instanced by Dispersoid Selenium," now in state of preparation for the *Kolloidchem. Beih.*; s. Reference No. XXV), that, with not excessively large aggregation, the precipitation curves may, in such cases also, be expressed by hyperbolic equations: *e.g.*, $— C^{\frac{1}{3}} .l = \text{const.}$, where l is the edge of a cube.

12. I have borrowed Figs. 15 and 16 from the very excellent book by C. P. Steinmetz, "Engineering Mathematics," pp. 230-231, Third Ed., Second Impression, McGraw-Hill Book Company, New York, 1917. The Fig. 17 is from the notorious paper by O. Lummer and E. Pringsheim. *Verhandl. deutsch. physik. Ges.*, 1, 230 (1889); 3, 36 (1901). See also: *Annalen der Physik.*, 4, Folge. 6, 199 (Fig. 1), and 200 (Fig. 2), 1901.

13. See: P. P. von Weimarn. References: No. XVIII and No. XXII. *Koll. Zeit.*, **4**, 138 (1909).

14. See: P. P. von Weimarn. References: No. XVIII, *Koll. Zeit.*, **4**, 137 (1909).

15. P. P. von Weimarn, *Koll. Zeit.*, 5, 155 (1909); 6, 32 (1910), and so on.

16. I have developed this view many years ago, and pointed out its correctness on more than one occasion since that time; and still, but few of my colleagues have thoroughly comprehended it. The Italian scientist Leonardo Cassuto (see his work: "Lo stato colloidale della materia," Pisa, 1911, pp. 252-253, 262-263; German edition: Verlag von Th. Steinkopff, Dresden, 1913, pp. 221-222,

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* The present paper has been written by the Author, in Russian, during the last three months of the year 1923; the English translation has come to hand, with the Editor's, in March, 1924. On reading the proofs (end of November, 1925) the Author has confined himself to merely the introduction of some insignificant improvements in the text, and to but a few alterations and additions in the bibliography.

230-231) is to be named among the first to give full appreciation to my interpretation of the question.

17. For details see: P. P. von Weimarn, T. Shohara and S. Takashige, "Adsorption, Dispergation and Solution." Now in state of preparation for the *Kolloidchem. Beih.*, s. Reference No. XXV. Compare also: P. P. von Weimarn, *Koll. Zeit.*, 33, 241 (Fig. 1), (1923).

17a. About the factors stipulating the formation of network jellies, s.: P. P. von Weimarn, *Journ. Russ. Chem. Soc.*, **40**, 1787 (1908); *Koll. Zeit.*, **5**, 122 (1909); **6**, 182 (1910); **9**, 25 (1911); *Journ. Russ. Chem. Soc.*, **46**, 610, 624 (1914); **47**, 2163 (1915).

18. P. P. von Weimarn, "Kolloides und kristalloides Loesen und Niederschlagen," p. 245 (Figs. 90 and 91: $SrSO_4 . xH_2O \rightarrow SrSO_4 + xH_2O$). Kyoto, 1921.

19. P. P. von Weimarn, "Kolloides und kristalloides Loesen und Neiderschlagen," § 43 (257-264; with three tables appended, describing the course of the gelatination process), Kyoto, 1921. The same takes place on preparing cellulose jellies in solutions of neutral salts, and so on.

20. For particulars, see: P. P. von Weimarn, "Kolloides und kristalloides Loesen und Niederschlagen," Kyoto, 1921, pp. 244-249, where instances are cited and microphotographs given of such "pseudo-colloid" jellies.

21. For more detail, see P. P. von Weimarn and S. Morishima, *loc. cit.*

22. For particulars, see P. P. von Weimarn and S. Morishima, *loc. cit.*

23. P. P. von Weimarn and A. L. Stein; see also "Kolloides und kristalloides Loesen und Niederschlagen," p. 41, Kyoto, 1921.

24. See *e.g.*, P. P. von Weimarn, *Kolloidchem. Beih.*, **4**, 125 (1912); 188 (1913).

25. For more details concerning the dispergation process, and most particularly, the connection between dispergation and adsorption, see "Kolloides und kristalloides Loesen und Niederschlagen," pp. 541-638, Kyoto, 1921; to what has been communicated in the text, this much should briefly be added: (1) With decreasing solubility of the dispergator its dispergation capacity (*other conditions being equal*) decreases (for an example: AgJ dispergated by KJ in alcoholic-aqueous medium with progressively increasing alcohol concentration, see "Kolloides und kristalloides Loesen und Niederschlagen, Table IX, pp. 562 and following, Kyoto, 1921). (2) The dispergation capacity of the dispergators (*e.g.*, the extents of the domains of stable colloid $BaSO_4$ solutions, with $BaCl_2$, $BaBr_2$, BaJ_2 as dispergators) increases with the increase in solubility of the dispergator, *other conditions being equal.*

26. For more details, see P. P. von Weimarn, *Koll. Zeit.*, **33**, 238-241 (1923).

27. Concerning the preparation, in agreement with my theory, of crystalline microspherites of gelatin, see the papers by Samuel Clement Bradford, "On the Theory of Gels," I-IV, *Biochemical Journal*, **12**, 351-381 (1918); **14**, 91-93 (1920); **15**, 553-562 (1921); **17**, 230-239 (1923).

28. P. P. von Weimarn and J. B. Kahan. See P. P. von Weimarn, "Kolloides und kristalloides Loesen und Niederschlagen," Kyoto, 1921.

29. Though issued in the form of a book in 1914, this work had originally been written by me in 1907, and appeared in *Koll. Zeit.*, 2-5 (1908-1909). As certain parts of the publication in *Koll. Zeit.* were not included in the book, I must refer the readers who are interested in the theoretical side of the question, to the above publication in *Koll. Zeit.*, **2**, 199-208, 230-237, LII-LXI (1908).

The Mesomorphic States of Matter

By G. Friedel, University of Strasbourg *

O. Lehmann, who as far back as 1889 drew attention to these new forms of matter, gave to them the unfortunate name of liquid crystals. It was believed, and many people still believe, that the distinction between these new types and the crystalline type was nothing but a difference in degree of fluidity.

I should like to show that the discovery of Lehmann is much more important than this and that he has unwittingly and at one stroke discovered two of the four general types of organization now known in matter.

Before the discovery of Lehmann all known matter was classified (as regards to structure) in either of two classical types: crystalline or amorphous. Of course other classifications suggest themselves if we take other points of view. Considering cohesion especially we may distinguish the solid, the liquid and the gaseous state, and varieties in each of these states. But what gives an altogether particular importance to the distinction between the crystalline and amorphous states is that in passing from one to another of these states of matter, we always find a *discontinuity*. For all other imaginable distinction *natura non facit saltus;* nothing but continuous transitions are met. Between the crystalline and amorphous states *natura facit saltus.* This demands explanation.

Crystalline substances are primarily characterized by the existence of "vectorial properties" which vary with the direction in a discontinuous manner and reveal the internal existence of a number of planes whose directions are related by the law of Haüy. These properties for the moment are five in number: (1) The limitation of crystal in its growth within a fluid, by planes; in other words the discontinuity of the variation of rapidity of growth with direction. (2) Cleavage; in other words the discontinuity of variations of cohesion with direction. (3) Twins. (4) Slipping. (5) Last but not least, diffraction of the X-rays.

The law of Haüy, which coördinates the directions of the planes revealed by these properties, can be expressed thus: The planes revealed by the properties exhibiting discontinuous variation, are among the grouped recticular planes of a certain network of parallelipipedons, and are the same for all properties in any one crystal.

It is from these discontinuous properties and from these alone, that we have deduced the structure of crystalline matter, which is *periodic:* The constituent units (we know to-day, thanks to Laue and Bragg, that they are atoms or ions) are regularly distributed in space according to certain intervals. Neglecting very small oscillations due to the thermal agitation, they occupy positions determined by their mutual affinities. Any definition of crystalline matter which does not take cognizance of the unquestioned fact that there exist properties subject to discontinuous variation and the law of

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* Translated by Miss M. N. Conklin, New York

Haüy, is deficient because it neglects an essential. No more need be said here, for it is generally admitted that crystalline matter is experimentally characterized by the existence of properties varying vectorially in a discontinuous manner and manifesting itself along planes related by the law of Haüy; and according to structural theories, by a regular or periodic repetition of the atomic units.

All crystals heretofore known are solid; sometimes they are more or less plastic, that is, they have an elastic limit beyond which permanent deformations are possible. But none of them approach a state that can be termed fluid. In other words the solid state alone seems to be compatible with the strict order that reigns in the crystal.

In opposition to crystalline matter, amorphous matter, which does not show a single vectorially discontinuous property, is in itself, apart from deformations due to external causes, isotropic in all of its properties. For this reason, and also because it is very frequently fluid (ordinary liquids, gas) which is hardly compatible with the idea of a definite spatial repetition of units, we are led to regard its homogeneity and its isotropicity as purely statistical and its structure as governed only by the laws of chance. In contrast to the perfect order which reigns in crystals, amorphous bodies represent perfect disorder.*

From the point of view of cohesion, amorphous bodies exhibit all states: gaseous, liquid and more rarely solid too, with (glasses) sometimes a rigidity that can be as great as any kind of crystal. Between these states there are no natural limits, no discontinuity. The apparent discontinuity between the liquid and the gaseous state resolves itself into a continuity if the curve of saturated vapor is not crossed.†

But is there not a discontinuity between the solid and the liquid state at the melting point? And what is the melting point?

THE "MELTING POINT"

To this question I shall answer positively this: the expression "melting point," which every one believes he understands, is a deceptive word which merely beclouds a lucid notion, and should be abandoned.

Let us consider a body having a definite melting point, sodium chloride for example: Cold, it is crystalline and solid. Raise its temperature; at 776° under atmospheric pressure it fuses showing an absolute discontinuity, and a sudden change of all its properties. Above this temperature it is amorphous and liquid. It is said that at 776° it has traversed the "melting point" and this unfortunate expression implies that the important phenomenon, which really corresponds to the discontinuity, is the passage from the solid to the fluid state. In reality, however, two things occur: (1) Passage from the crystalline to the amorphous state. (2) Passage from the solid to the liquid state. Are these two events always simultaneous? And if they are not always so, which one of the two is accompanied by discontinuity?

Let us take, with Mügge, the example of the feldspars orthoclase and albite, or, according to recent researches, that of quartz. These bodies, crystalline and solid at an ordinary temperature, at a certain temperature *t*, quite below that at which they fluidify, transform discontinuously and suddenly become amorphous, at the same time keeping their shape. Above this temperature they have become amorphous but remain in a state that can only be qualified as solid. When afterwards the temperature is gradually raised above *t*, this amorphous matter, this glass, passes by gradual transitions without any kind of discontinuous limit, from the solid to the liquid state, exactly as do ordinary glasses. What is most singular in these cases is that at the temperature where the discontinuous passage is made from the crystalline to the amorphous state, the amorphous glass which results from this transformation is still solid. Therefore in this case the phenomenon of the "melting point" is duplex and the temperature *t*, to which this name is given, shows itself in its true light. It does not correspond to the passage from the solid to the liquid state which is essentially continuous, but to the passage from the crystalline to the amorphous form. The name "melting point" is most inappropriate to describe such a point. *Amorphorization point* would be more correct. Thus the discontinuity, the natural limit to which the name "melting point" has wrongly been given, is in reality that of the passage of the crystalline to the amorphous form. As these amorphous bodies are generally fluid and very rarely solid, it happens quite often that this transformation is accompanied by a sudden passage from the solid to the fluid state, especially when the temperature is high. But discontinuity is not involved in that change. It characterizes the change of structure. In no case is it possible to pass from the crystalline to the amorphous form without traversing a discontinuity which involves a profound alteration of the molecular structure: Passage from *crystalline order* to *amorphous disorder*. This passage takes place either under increasing thermal agitation (increasing temperature) or as the result of dilution (solution). Mügge has recently shown that it can be determined by another cause, namely, the very prolonged bombardment by α rays; but in what follows we have only to consider the first two causes.

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* Many crypto-crystalline substances have in error been called amorphous—metals for example. J. A.

† See paper by J. Alexander, this volume. J. A.

Remember that the same body can present several different crystalline forms. They change from one to the other only by discontinuities quite like the amorphization point.

The importance and the true sense of the discontinuity that is observed between the crystalline and the amorphous states has led us to see that between the crystalline order and the amorphous disorder there exists not continuous transitions but two intermediary types of partial order, different in themselves and differing from the two types formerly distinguished by discontinuities. They are the *mesomorphic states*, comprising the *smectic* (∂μῆγμα, soap) and the *nematic* types (νῆμα, thread). Let us take, for example, one of the rather rare substances in which the series of four states is complete, cholesterine caprate. Cold, it is crystallized and solid. Raising the temperature, at $T_1 = 55.5°$ we observe a discontinuous transformation, reversible, altogether comparable to that of the ordinary point of amorphization of the crystals. Above this temperature the body is pasty, between solid and liquid; but it is not an amorphous body. It is quite a new type of matter, anisotropic, birefringent, which we shall call the smectic state. Then as the temperature steadily rises a new discontinuous transformation takes place at $T_2 = 68.5°$ which is somewhat like a second "melting point," and the substance changes to a new state quite different from the preceding one, and which, also, is not amorphous but anisotropic and birefringent. In most substances this new state is very fluid; here it is still quite pasty. We will call it the nematic state. Finally at $T_3 = 85°$ there is a third discontinuous transformation, a third "melting point" and transition to a fourth state which this time is an ordinary amorphous liquid.

With the majority of substances that exhibit these mesomorphic states and which are moreover rather exceptional bodies of a special chemical type, there exists between the crystalline and the amorphous phase but one of these two phases, smectic or nematic. But when the two exist, they always present themselves without exception in the same order. With increasing temperature the following is the succession:

Up to T_1 Crystalline Form (one or many).
Between T_1 and T_2 Smectic Form.
Between T_2 and T_3 Nematic Form.
Above T_3 Amorphous Form.

Cases have been described where there might exist more than two mesomorphic forms. This is not impossible. But in all cases that I have been able to examine I have verified that the different forms of a same phase have been mistaken for distinct phases. For the same reason many substances have been described as having two "crystalline liquid" (mesomorphic) phases, when they have but one. I think, unless there is proof to the contrary, that there is never more than one smectic and one nematic phase, and when the two exist, the smectic phase has always its domain of stability at lower temperature than the nematic phase.

A very important point is that mixtures offer exactly the same smectic and nematic structures as do pure substances. In mixtures, be they what they may, there is never observed any intermediary state, no gradual passage from one to the other of the four states. Even while mixing ordinary crystalline and amorphous substances in all proportions and at all temperatures, nothing is ever observed but crystalline or amorphous matter and nothing which might be intermediate between these two types. Even when substances having mesomorphic phases are in question, nothing is ever seen but crystalline matter, smectic matter, nematic matter or amorphous matter. The two new states reveal themselves, therefore, as constituting altogether general types of matter, more rarely realized than the other two and pertaining to certain special chemical compounds, but as perfectly defined and delimited as the crystalline or amorphous types.

Just as in the passage from the crystalline state to the amorphous, dilution as well as increase of temperature, can determine the transformation of one into the other of the four states. The 10-bromphenanthrene-6-sulfonic acid of Sandquist is crystalline at ordinary temperature, and is anhydrous. When increasing proportions of water are added to it, without changing the temperature, it passes suddenly to the smectic state; then with a greater quantity of water to the nematic state; finally upon still greater dilution to the amorphous state of an ordinary solution. Each one of these transformations exhibits a perfect discontinuity and there is a sharp limit between the several phases. A variation in the temperature changes this limit in a continuous manner, which indicates clearly that it is not a matter of definite hydrates. It is the continual variation in the quantity of water which, as well as the variation in the temperature, determine, for certain content, the intermittent transformation of one into the other of the four types of organization. An example of the same phenomenon, less complete but connected with better known substances, is met in soaps, which are "smectic" at ordinary temperature when they contain but little water, but which, when the quantity of water increases, pass suddenly, at a certain content, which is a function of the temperature, to the state of an amorphous solution. The importance and the nature of this transformation seem to have been generally ignored by authors who have experimented with solutions of soaps.*

It may also be noted that if, in the state of dilution, the solution of soap is a colloid, the same designation must be applied for the greater state of concentration where the soap imposes on the mixture of water and soap its smectic structure. If, as seems reasonable, we understand a colloid to be a mixture of, at least, two phases, in which one of these phases is dispersed in very small units, there are colloids having each one of the four structures. There are amorphous "colloids," which are the ordinary "colloidal" solutions or ordinary gels—the dispersed units may moreover be crystalline as in gold sols, for example. There are "colloids" with nematic structure, as Sandquist's acid mixed with water, between certain limits of concentration. There are colloids with smectic structure, as the same acid in a greater state of concentration or as the concentrated solution of soap. There are finally substances that may be regarded colloids having crystalline structure. These are, for example, the zeolites, in which the predominant silicate molecule imposes its periodic structure, while water associated in continuously variable proportion, enters the space lattice without participating in its stability. A gold sol is a dispersion of crystalline units in predominating amorphous liquid, which imposes on the ensemble its amorphous structure; so the other extreme, a zeolite, is a dispersion of amorphous elements (water) in a predominant crystalline substance which imposes on the mass its crystalline structure.

The unquestionable existence of mesomorphic colloids, *e.g.*, concentrated solution of soap, justifies the introduction in this work of some remarks on mesomorphic states.

So far as concerns the chemical composition of all substances exhibiting mesomorphic phases, they are organic compounds with complicated molecules. Lehmann erred in including with them silver iodide under the cubic form which it takes above 146° and which is simply crystalline, not liquid at all, without any of the characteristic structures of the mesomorphic substances. The chemical behavior of substances with mesomorphic phases is most diverse. Only one condition, after Vorländer, dominates, seems necessary and perhaps even sufficient. It is that the molecule be very long and rectilinear, without bifurcations or heavy side chains. In the case of disubstituted benzene rings the para compound alone gives rise to substances exhibiting mesomorphic phases; the meta compound rarely does so and then only when one of the substituted groups is small. The ortho compound never shows mesomorphic phases. It seems after all that the bodies with mesomorphic phases are simply those in which the molecule is very long and rectilinear, needle shaped, no matter what may be the other chemical characteristics. No difference in chemical nature is at present known between substances exhibiting the smectic phase and those exhibiting the nematic phase and the same substance may exhibit both phases.

Mixtures may distinctly show one or the other of the mesomorphic states which are not shown by the pure materials. They may serve just as well as do pure substances for studying the characteristics of both mesomorphic types, which we will now briefly discuss.

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* See paper of J. W. McBain, this volume. J. A.

SMECTIC STATE

Types: Soaps, when cold. Better still, as showing much more distinct structures, ethyl para-azoxybenzoate between 114° and 120°, ethyl para-azoxycinnamate between 140° to 250°. Generally smectic substances are pasty like soft soap, or solid like soda soap.

1. Homogeneous Areas.

Smectic substances may be obtained with homogeneous areas by fusing crystals between two glass slides. In this case each area is perfectly limpid, maintains the shape of the crystal from which it originated and shows itself birefringent (very strongly so with ethyl azoxybenzoate or the azoxycinnamate). Without exception the optical character is uniaxially positive, the optic axis being regularly directed with regard to the initial crystal. On the edges these areas are not, as in the case with crystals, separated by surfaces of discontinuity, but are joined by an infinity of minute figures which are called *focal groups,* identical with those to which we will later refer. (Fig. 1.)

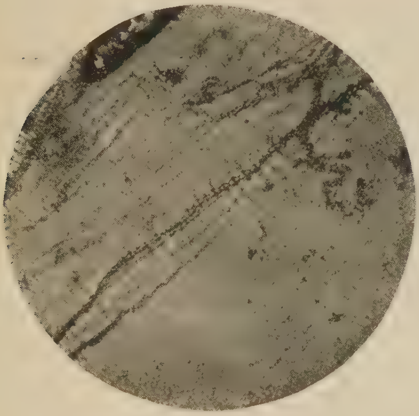

FIG. 1.—Ethyl azoxybenzoate — smectic edges formed by fusing crystals. Natural light, × 80. Each crystal has formed an edge which appears homogeneous centrally, and which fits into the neighboring edges by a marginal rim of focal groups. One of these limiting lines traverses the middle of the figure, and clearly shows the focal groups stretching obliquely.

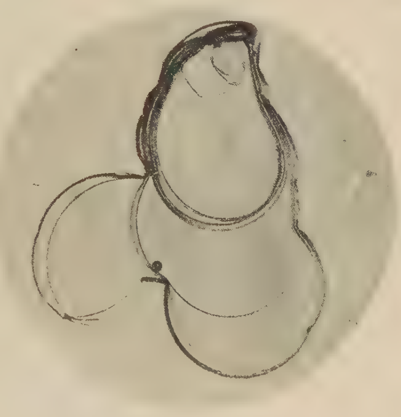

FIG. 2.—Natural light, × 25. Ethyl azoxybenzoate, with a small amount of ethyl azoxycinnamate added. "Terraced drops" formed on a cleavage plane of mica.

Homogeneous areas may also arise by *homeotropism,* that is to say by the spontaneous orientation of the optical axis normally to the surface of the preparation. This orientation has been erroneously attributed by Lehmann to the action of the glass. That this is not so is proven by putting some of the substance in suspension on a small circular hole 1 mm. in diameter, for example, pierced in a thin plate of glass; it will show better than in any other case the normal orientation at the surface.

Homeotropism is due to the orienting action of the superficial pellicle of the liquid itself. The glass opposes that orientation only when there is intimate contact between the liquid and the glass itself. So the movements of glass aid homeotropism in destroying the adhesion of the liquid to the glass.

The most perfect forms are produced by homeotropism when the smectic substance does not come into contact with the transparent support, either on a hole, as mentioned above, or, as Grandjean has shown, in the very curious phenomenon of *terraced drops* (Fig. 2). To observe these terraced drops it is necessary to employ for transparent support a cleavage plane freshly separated from a crystal which does not exercise on the liquid any selective orientation. Mica serves quite well for the two types named above, or their mixtures. Upon melting a little fragment on the mica without going above T_2, it takes the shape of a drop of which the superior surface is strictly flat, forming a great number of flat terraces, limited by smooth curves of various shapes. These terraces slide with the greatest facility over one another. They vary greatly in thickness and generally many more of them are seen under higher magnification. The optical axis is normal to the plane of the terraces. At the edges of each terrace there is a sudden change of level and there appears an infinite number of small focal groups, the structure there ceasing to be homogeneous.

There is a close analogy between terraced drops and the terraced plates long ago observed in soap bubbles; these were studied with precision by J. Perrin, who also measured their thickness. These soap plates do not arise from an ordinary amorphous liquid, but are rather plates of a smectic substance. Under one or the other form these terraces normal to the optic axis demonstrate the existence, normally to this axis, of a plane which in the structure of the substance plays a very peculiar rôle. The measurements of Perrin and Wells gave a basis for the belief that the molecules of smectic substances are disposed along equidistant planes, which according to Wells, are in the case of potassium oleate 44 Å. U. apart. Many other characteristics of smectic substances are in accord with this hypothesis, as we shall see.

2. Conic Structures.

Whenever a smectic substance is not in homogeneous areas, it assumes a conic structure. This is the case, for example, when starting with the amorphous state, the smectic state is reached by lowering the temperature. The same structure appears, furthermore, as uniting homogeneous areas.

In this condition the smectic substance shows itself in ordinary, as well as in polarized light, crossed by a great number of black filaments that could be taken at first sight for solid threads (Figs. 3 and 4). These filaments all have the shape of ellipses and of branches of hyperbolas. Often too fine to be made out in detail, these peculiar geometric figures can, by the use of some precautions, be obtained large enough to be studied in a very thorough manner. To each ellipse or arc of ellipse there corresponds the arc of hyperbola, and these two conic sections are related to each other focally, that is to say, their planes are rectangular, their centers coincide, and each passes through the focus of the other. To each one of these focal groups corresponds a domain whose structure it dominates and which is limited by the four cones of revolution having as apexes the extremity of one of the conic sections and resting on the other. If, as very often happens, the ellipse is complete, only two cones appear.

These focal domains are adjusted to each other according to a very definite geometry, very peculiar at first blush, which cannot here be considered in detail. It is based on this simple principle that two focal domains never penetrate each other and when they do touch are mutually tangent along a generative of the cones which limit them.

During the passage from the smectic state to the crystalline state, it sometimes happens (cholesterine stearate, cholesterine myristate, various mixtures) that the extremely fine crystals are oriented by the smectic substance and disposed in small plates, at each point of the mass, normally to the optical axis of the liquid (Figs. 5 and 6).* On returning to the smectic state the inverse orientation reappears and the conic sections reappear in their former places, without change (Fig. 7). The study of these "pseudomorphoses" of smectic substances with conics aggregated like little crystals, in which the conics are thus kept in a solid state, and where the small crystalline plates delineate the outline of the optical axis, just as iron filings indicate the lines of force of the magnetic field, has enabled us to understand the structure of the focal domain. It is a region of the mass in which at each point the optic axis rests on the two focal conics. In other words the surface normal to the optical axis which is a plane in the homogeneous structure is, in the focal domain, what the mathematicians call a *Dupin's cycloid*. A focal domain is simply a little region in which the optical axes meet two curves. Mathematicians have proven that the normal surface to the optical axis, the one corresponding to the planes of the terraced drops, is perforce a Dupin's cycloid, and the two curves are necessarily focal conics.

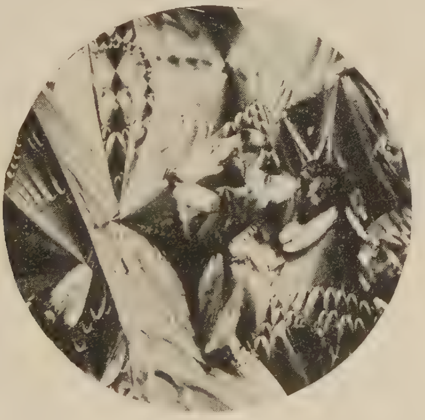

Fig. 3.—Taken with crossed Nichols, × 25. Ethyl azoxybenzoate, thick specimen with the lower surface in focus, showing "conic structures."

We see now why two focal domains cannot interpenetrate. There cannot at the same time be two structures at the same point. And the fact that they are mutually tangent shows that, throughout the liquid, there is no discontinuity other than that produced at the conics. While in crystalline matter, the homogeneous crystals are separated by *surfaces* of discontinuity, in smectic matter there are only *lines* of discontinuity, which are the conics. These conics are curves towards which the optic axes converge. They are, consequently optical discontinuities. This explains in great detail the manner in which these curves are manifested, more or less sharply defined according to conditions; it also explains why, when they have the conical structure, smectic substances are cloudy. They oppose the direct passage of light rays, an obstacle of the same sort as that formed by an agglomeration of small birefringent crystals turned in all directions. But, whereas in crystalline substances the refractions are produced at the separate surface of the crystals in smectic substances they take place when the ray passes in the vicinity of a conic where the optical axis changes its direction abruptly. The cloudiness of smectic substances obtained without precautions, which has given rise to many absurd statements about "liquid crystals" and led to their being considered as suspensions or emulsions, is therefore completely explained. The same applies to nematic substances.

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* Fig. 5: mixture of ethyl azoxybenzoate and of azoxycinnamate smectic state. Fig. 6: same preparation, solidified, crystallized state, pseudomorphous with the smectic substance. Fig. 7: same preparation after return to smectic state.

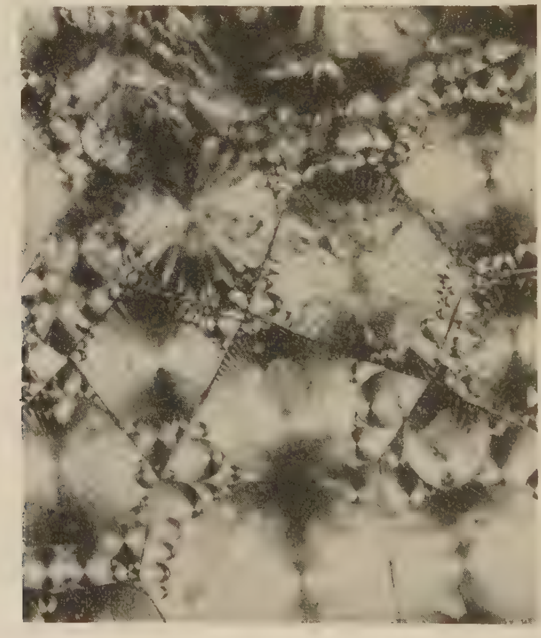

FIG. 4.—Nichol polarizer, without analyzer, × 80. Ethyl azoxybenzoate, showing typical "polygonal" structure, in which every focal group has one of its conics at the surface.

The fact that, in the focal domain, the surface normal to the optical axis takes the form of a Dupin's cycloid, tends to confirm the hypothesis of a structure at equidistant surfaces because a group of cycloids corresponding to the same conics, constitutes an ensemble of parallel surfaces at all points equidistant. The arrangement of these focal areas among themselves has, in certain cases, been followed down to groups of very small dimensions which appear especially near the surface where it exhibits change in curvature. By the mere combination of these more or less eccentric focal areas, there are formed designs of extreme delicacy, fans or feather-like forms, very characteristic of smectic substances; and this permits them to be recognized even in cases where the conics are too small to be clearly made out.

Fig. 5, 6, 7.—Natural light, × 80. Mixtures of ethyl azoxybenzoate and ethyl azoxycinnamate—thick specimens.

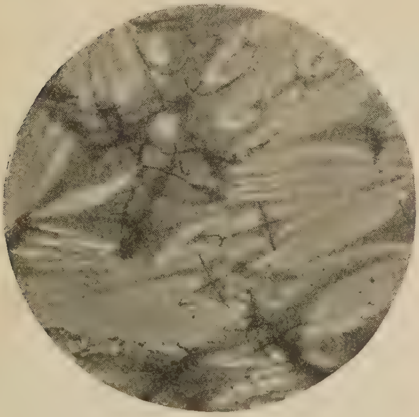

Fig. 5.—Smectic state, conic structure.

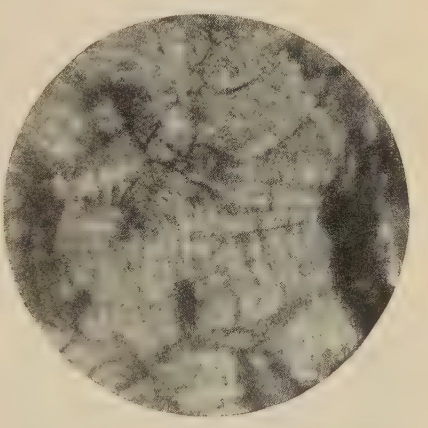

Fig. 6.—Same specimen, after chilling; solid crystalline condition. The fine crystalline layers are at each point oriented normally to the optical axis of the smectic substance, making "pseudomorphs" of focal groups. The mixture, somewhat too rich in azoxycinnamate, has on cooling separated into two phases, one of which (the two darker masses to the right and the left) has not developed the phenomenon and disturbs somewhat the structure of the other.

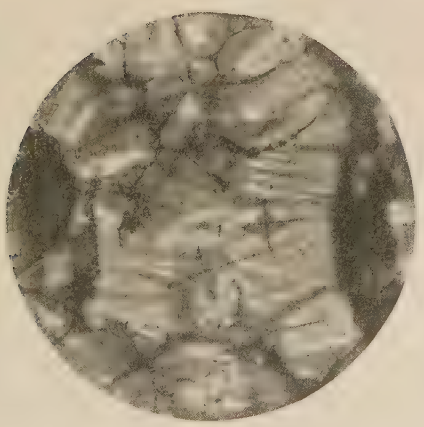

Fig. 7.—The same preparation, after re-heating and returning to the smectic state. The two masses above referred to persist, which shows that Fig. 7 and 5 are not the same. Nevertheless, the focal groups of Fig. 5 are once more seen at the same points. The smectic phase has re-formed on the crystalline phase of Fig. 6.

3. Little Rods.

Starting with an amorphous substance, if we cool below the point of transformation into the smectic form, the smectic phase appears as curious little rods resembling balusters, whose bulgings are decorated with lines of little beads, and ornamented with fine focal groups. These little rods, all statements to the contrary notwithstanding, never have a crystalline form. Even the number of beads about their bulgings is purely random, sometimes 3, 4 or 6, which has led to the belief of a ternary, quaternary or senary symmetry comparable to that of crystals; but just as often and with the rodlets of a same preparation 5, 7, 15 or 20—in fact any number. The internal structure is conic, exactly as in the larger masses. There is no basis for attributing to these small bodies the periodic structure of crystals. As in the forms described above they show discontinuous properties only along one plane, which is the plane normal to the optical axis. The mere fact that they are not spherical shows that the capillary constant of their contact with the amorphous phase varies with the direction. Now the study of crystals leads us to consider the variations of the capillary constant as being dependent primarily upon the spatial distribution of the atomic or molecular units. This is therefore an additional and cogent reason for believing that in the structure of the smectic substances, we are confronted with a spatial distribution of molecules and it confirms the idea that these molecules are distributed on equidistant surfaces. Nothing like this exists in nematic substances whose drops are spherical.

Instead of the crystalline forms that he first imagined he saw in the rodlets, Lehmann thought it possible to describe as twins certain bent (or elbowed) rodlets that are sometimes formed by the union of two straight rodlets. These imaginary twins are nothing but rodlets whose structure is dominated by a principal focal domain whose hyperbola has a sharp curvature. They have no connection with crystal twins.

4. Orientation by Crystals.

Many crystals orient certain smectic substances. This is not a question of homeotropy, which, as we have seen, accompanies an imperfect contact; on the contrary the smectic substance in contact with a freshly cleaved crystal plane is oriented by this plane so that its optical axis, which seems always to place itself parallel to the cleavage plane, takes definite directions relative to the crystallographic axes of the support. This orientation like that of crystals by crystals, is essentially selective as Grandjean has shown. It is furthermore more frequently realized than is the case with crystals.

Study of the mutual orientation of different species of crystals, shows that these orientations are possible only when there is harmony between the periods of the two species. This phenomenon, which is very closely related to twins and so isomorphous syncrystallization, is governed by a general law which applies also to these collateral phenomena. A prerequisite to mutual orientation is that the two lattices (single or multiple) of the two species have, within a certain limit of tolerance, the same form and same volume. That is why orientation is selective, orientation, which is a form of continuation of growth, being impossible when the two periods are not properly matched. That the same condition exists for all smectic substances in their orientation by crystals leads us to believe that in smectic substances there is something periodic, and that the period must match that of the crystal in order that mutual orientation may be possible—an additional confirmation of the view of the distribution of molecules along equidistant parallel planes.

5. Rectilinear Flows.

A very curious phenomenon, discovered by Grandjean (Fig. 8) is the following:

When a small fragment of a substance whose smectic phase is oriented by a crystal, is melted on the fresh cleavage plane of the crystal, this fragment in passing into the smectic state, flows out to make projections in the shape of small rods which are sometimes quite long and have rectilinear edges always aligned normally to the optical axis, the edges being parallel to the crystallographic directions of the support. At the surface, which is curved, there are ornamentations by fine focal groups forming "feathers" (Fig. 9); but the mass is homogeneous and the optical axis is normal to the alignment of these curious drops. From this it is obvious that, as was the case with the terraced drops and also with the rodlets previously referred to, the fluidity of smectic substances is much greater in the direction of the plane normal to the optical axis than in the direction of this axis. It might almost be said that the substance is liquid in the former direction and solid in the latter.

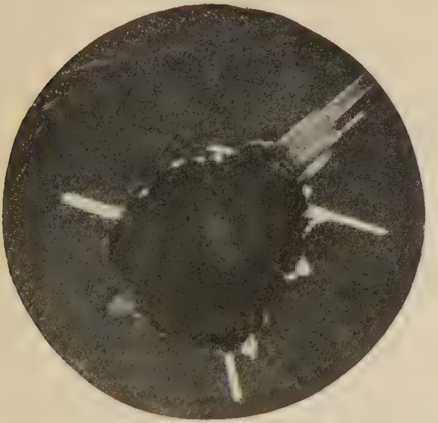

Fig. 8.—Crossed Nichols, × 80. Fragment of ethyl azoxycinnamate crystal, in course of melting to the smectic state on a sliver of talc. Note the three rectilinear directions of flow of the smectic phase, at 60 degrees to each other. One of these flow-lines has been brought near to extinction to show the transverse stratification.

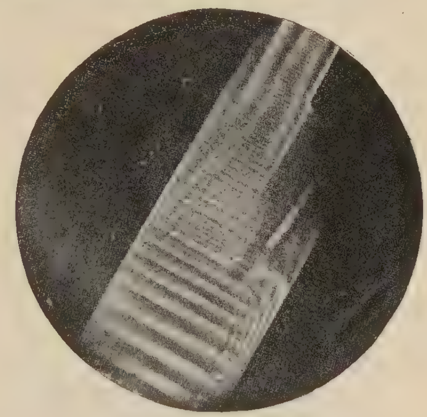

Fig. 9.—Crossed Nichols, × 80. More highly magnified detail of a flow-band of Fig. 8, showing that the transverse stratification is due to the presence of superficial focal groups.

All these properties indicate that smectic substances have the following structure:

The very long rectilinear molecules are oriented in such a manner that their rectilinear axes of alignment are parallel. Around this direction they are furthermore turned in a random manner, whence arises the symmetry of revolution manifested by uniaxiality. In another way they dispose themselves by successive equidistant strata; in each of these strata they have no regular spatial distribution, but there exists in smectic substances something of the perfect periodicity of a crystal—that is, this single direction of equidistant planes, in a certain measure analogous to the recticular planes of crystals.

This hypothesis advanced on the basis of the reasons above mentioned, has received full and complete confirmation by X-ray diffraction tests carried out on soaps by M. de Broglie and G. Friedel. The plane normal to the optical axis reflects X-rays of sufficient wave length exactly as do the reticular planes of crystals. But here there is but one reflecting plane. They have measured by this means the distance between the planes of sodium oleate which is 43.5 Å. U. in excellent accord with the measurements of Perrin and Wells.

It must therefore be considered that the stratified structure of smectic substances is proven. It can be seen how far wide of the mark it was to call these bodies "Liquid Crystals." This gave no idea of their properties nor of their structure, so different from those of crystals. They constitute an entirely distinct type of organization of matter.

NEMATIC STATE

We must here distinguish two types that we shall call the true *nematic* and the *cholesteric* type.

True Nematic Type.

These are substances without rotatory power. Examples: Para-azoxyphenetol between 135 and 165°, Para-azoxyanisol between 116 and 133°.

Very often nematic substances are liquid, sometimes as fluid as any other kind of amorphous liquid. They can therefore pass through all degrees of consistency more or less solid without undergoing any change of structures.

1. *Homogeneous areas.*—As in the smectic state, it is possible, by taking suitable precautions, to obtain large homogeneous areas by fusing the crystals between glass slides. These areas, whose limits are those of the initial crystals, are in this case too always positively uniaxial. But they differ greatly in character from the analogous areas of smectic substances.

Firstly, the nematic liquid, when it is quite fluid, is in continuous motion, without showing any change in its birefringence. Between Nicols they appear to be large entirely stationary crystals having their directions of extinction, their birefringence (enormous in the two substances referred to) perfectly constant, and yet it can easily be seen that all kinds of tides may sweep over these areas. Again and again molecules which enter an area instantly acquire the orientation that characterizes this area. Nothing similar exists in smectic substances.

The orientation of each area is determined by the two superficial pellicles adherent to the glass, which confine the preparation. In certain substances, *e.g.*, the two mentioned, these pellicles are of extraordinary persistence, even at a temperature where the mass has long since passed over either to the amorphous or the crystalline state. For in returning to the smectic state after fusion, for example to an amorphous liquid, these areas are found at the same places with the same limits and the same optical properties. This persistence of superficial pellicles varies greatly, however, from one substance to another.

Upon displacing the two glasses with respect to each other, the areas practically double, each one of the pellicles sticking to its glass (Figs. 10-11).* Then, whether the glasses have turned with respect to each other or not, whenever an upper area overlaps one of another orientation, there appears a *twisted* area. The curious optic properties of these areas, described by G. Friedel and Grandjean, have been explained by Mauguin. They show that the liquid in its mass connects the two pellicles with an even helicoidal torsion. And this, it must be recalled, in a liquid which is or may be constantly agitated and whose molecules at each point renew themselves ceaselessly. This is not one of the least surprising facts presented by the world of mesomorphic substances, so marvelous and so rich in surprises. The torsion here mentioned must not be confused with mechanical torsion, for a twist of 360° is here equivalent to no torsion at all.

Figs. 10-11.—Crossed Nichols, × 25. Azoxyphenetol, between glass slides treated with hydrofluoric acid.

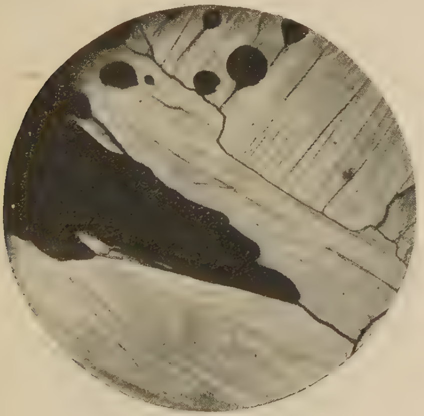

Fig. 10.—Firm crystal border.

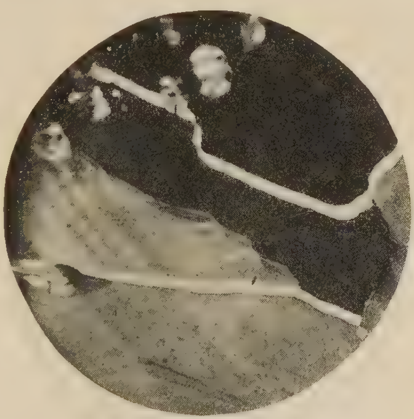

Fig. 11.—The same preparation, melted to the nematic state, after slight relative displacement of the glasses. Each crystal border has given rise to a homogeneous nematic border. The displacement has produced a double limit to the borders, one being attached to the lower glass, the other to the upper glass. Between these limits there are now twisted borders.

Homogeneous areas may also arise by homeotropy, exactly as with smectic substances. This is, in fact, a property which is also found in soft crystalline substances and which is not peculiar to mesomorphic bodies. Homeotropy is often spontaneously produced at a certain temperature and has created the belief that a new phase has appeared.

Nematic substances never exhibit terraced areas.

2. *Thread structure.*—When they are not in homogeneous areas, nematic substances assume a special structure which corresponds to the conical structure of smectic substances. This is the thread structure that is sometimes observed pure alone, and occasionally associated with homogeneous areas in

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* Fig. 10—Crystalline azoxyphenetole. Fig. 11—The same preparation in nematic state, after a small relative displacement of the glass slides.

a more or less confused manner. Visible in natural light as well as between Nicols, black threads can be perceived in the mass and they look like the conics of smectic substances, but have no simple geometrical form. These threads, as Grandjean has shown, are axes of revolution of the structure towards which the optical axes converge, or around which these axes revolve. Occasionally they adhere to the glass, and are thus immovable. Often they are fastened only by their extremities, and in this case, carried by the movements of the liquid, they become deformed, lengthen or shorten themselves continuously. When they are entirely immersed in the liquid they close up and form a ring which contracts and disappears without leaving any trace.

Difficult to study under this form on account of their mobility, the threads can be more closely examined in what may be called the *nuclear structure.*

FIGS. 12-13. × 80.

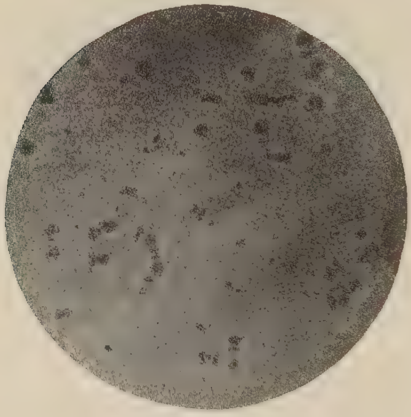

FIG. 12.—Natural illumination. Note two kinds of "complete nuclei": "fixed" nuclei, with a gray circular penumbra, and "twirling" nuclei, with a gray quadrangular penumbra having rounded angles. "Demi-nuclei" appear merely as black points.

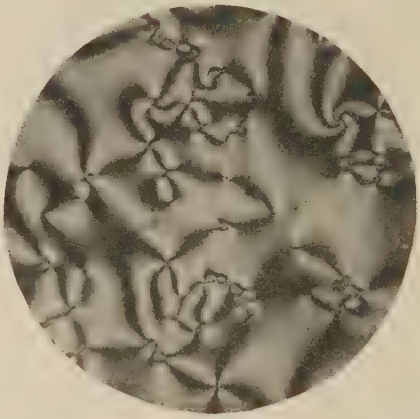

FIG. 13.—The same preparation, seen between crossed Nichols. The same nuclei are seen, but they now are united by black bands; and the complete nuclei are now seen (crosses with four arms), as well as the demi-nuclei (with two branches).

This structure is obtained by taking suitable precaution, and different substances vary in the ease with which it may be obtained. The threads dispose themselves normally to the preparation, fixed to the glass by their two extremities. They appear as small nuclei surrounded, in natural light, by a clearly defined gray area (Fig. 12) and showing between Nicols (Fig. 13) * two black brushes diverging from the center of the nucleus. From each of these, between Nicols, there run two or four black bands which, when the preparation is turned, sweep its whole surface and which connect the several nuclei. There are four kinds of nuclei. And as is the case with the conics of smectic substances, they are governed by a curious geometry, entirely different from that observed in smectic substances. There are in the first place nuclei with four branches (complete fixed nucleus) whose four branches when the preparation rotated between Nicols, remain fixed. Then there are others with four equal branches (complete rotatable nuclei) whose branches, when the preparation is rotated between Nicols, turn in the same direction and with double the angular rotation. In ordinary light, the former have a gray circular halo, the latter a square or rectangular halo with rounded angles (Fig. 12). In addition there exist two corresponding types of nuclei with only two branches, one fixed, the other rotating (demi-nuclei). If the former two types are designated + 2 and — 2, and the latter two + 1 and — 1, the following laws are observed:

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* Fig. 13—Same preparation as Fig. 12.

1°. Two nuclei or demi-nuclei, joined by a black branch, are always of contrary signs.

2°. If, by moving the preparation, nuclei are made to appear or disappear, the algebraic sum of their indices is always zero.

3°. Only those conjunctions are possible in which the absolute value of the sum of the indices is at the most equal to 2. And the result of the conjunction is given by that sum. Therefore, two complete nuclei of the same kind will never unite. But, on the other hand, the conjunction of a complete fixed nucleus with a complete rotatable nucleus, causes the disappearance of both $(+2-2=0)$; the conjunction of a complete fixed nucleus with a rotating demi-nucleus gives a fixed demi-nucleus $(+2-1=+1)$, etc.

There is here involved a geometry of arrangement resulting from the fact that the threads are axes of rotation of the structure, which has four different modes of rotation. About the complete fixed nuclei, the principal sections revolve in the same direction and at the same angle as does the vector ray issuing from the nucleus; around the complete rotating nuclei they revolve at the same angle and in an inverse direction. About the demi-nuclei they revolve only 180° for a whole turn of the vector ray in one direction or the other.

3. *Drops.*—When the amorphous state becomes nematic through lowering of the temperature, the nematic phase appears in the shape of drops which are always spherical, and no longer as rodlets, as is the case with the smectic phase. That is to say that the capillary constant, as is the case with amorphous bodies, does not vary with the direction. This leads to the conclusion that, as in amorphous bodies, the molecules have no regular spatial distribution, but are distributed at random.

4. *Orientation by crystals.*—In the numerous cases tried, nematic substances have always been oriented by any crystal. The orientation of the molecules of the nematic substance by the molecular field of the crystal is no longer, as with smectic substances, and still more markedly with crystals, limited by the matching of the two periods. This is further evidence that there is nothing periodical in nematic substances.

5. *Brownian movements of the optical axes.*—A curious property of nematic substances when they are sufficiently fluid, consists in this: When, by homeotropy, for example, there is obtained an area whose optical axis is normal to the preparation and which consequently appears black between crossed Nicols, this area is not uniformly black. It appears agitated by a perpetual scintillation of luminous points. Upon touching the cover glass the preparation is traversed by a lightning-like flash, the regular homeotropic structure being momentarily disturbed. This scintillation as Mauguin has shown, is merely the same phenomenon, though much localized, as that produced by thermal agitation. It increases when the temperature is raised and becomes imperceptible at low temperatures or when the viscosity of the liquid is too high. It is sometimes violent enough to be seen throughout the whole preparation even in the nuclear areas.

6. *Action of the magnetic or the electric field.*—A strong enough magnetic field orients nematic substances, so that the optical axis aligns itself parallel to the field. In the electrostatic field, the optical axis aligns itself normally to the field and there appears a vast number of threads parallel to the field. A magnetic field parallel to the optical axis diminishes or even stops the Brownian movement of the axis, evidently forcing the molecules to maintain their orientation better. Up to the present, no one has demonstrated any action of the magnetic field on smectic substances or on cholesteric-like substances, which no available field has as yet been able to untwist.

Considering these properties all in all, we are struck by the lack of the reasons which led us to conclude that smectic substances have a stratified distribution of molecules. Besides, the diffraction of X-rays, tried by different observers, has given entirely negative results. The high birefringence and the uniaxiality of nematic substances lead us to assume that with them, as with smectic substances, the molecules have a direction of common arrangement around which they occupy random azimuths. But the spatial distribution of the homologous points of these molecules is a haphazard distribution, as in an amorphous body. The nematic substance is, so to say, an amorphous substance whose molecules are mutually oriented in such a manner as to have a common direction, probably that of their length. This is in perfect agreement with what chemistry teaches us regarding the shape of these very long and rectilinear molecules. It is hardly imaginable how molecules in the shape of long needles could arrange themselves, so that the ensemble has the usual density, unless the long axes of the needles be parallel. Thermal agitation determines only oscillations around this position of parallelism. It is possible that, when the substance passes to the amorphous state, the molecules lose their rigidity and become all tangled up. This would explain the sudden increase of viscosity verified by Schenck in the passage from the nematic to the amorphous state.

L. Royer has shown that this structural hypothesis is confirmed by the application of Langevin's theory concerning magnetic birefringence, from measurements made on the indices of nematic substances. It seems then proved that the birefringence of the nematic substances, as well as that of amorphous liquids under the action of the magnetic field, is due only to the orientation of the molecules. The difference is that in magnetic birefringence the orientation is always very imperfect so that the birefringence is very small, while with nematic substances the orientation of the molecules under the action of the field, determined by their mutual actions, is almost perfect and the birefringence is considerable. It is all the more remarkable that the same theory explains two groups of facts whose order of size are so different.

I would again insist on the striking order which is introduced into this aggregation of facts so confused up to the present.

Let us start from the crystalline state usually found at low temperatures, in which the atomic or molecular elements are arranged in perfect order, almost immobile, thermal agitation results only in very minute oscillations around fixed positions. As the temperature, that is to say, the thermal agitation, increases, there comes a point where the crystalline order is broken. The molecules acquire one degree of freedom; they are, however, constrained to a distribution on equidistant surfaces * which still recalls to some extent the perfect periodicity of the crystal; but on these surfaces they no longer have definite positions, and this constitutes a first appearance of amorphous disorder: we have the smectic state. Then as the temperature increases again, there is another rupture of bonds; all regular spatial distribution disappears; from the crystalline order remains only the mutual orientation of the long axes of the molecules: we have the nematic state. Finally at a still higher temperature the thermal agitation has mastered all the bonds that determine the crystalline order, there is neither distribution nor orientation of the molecules: we have the amorphous state.

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* Somewhat like skaters on ice. J. A.

Cholesteric Type.*

This type, which is that of *negative* mesomorphic substances, has long remained an enigma. Now it is known to be a special form taken by nematic substances when their asymmetry is connected with rotatory power. The addition of a substance having rotatory power, to a nematic substance, transforms its nematic phase into a cholesteric phase and there is continuous transition between these two types.

Examples: The greater part of the cholesterine salts (but not, for example, the oleate or the stearate which have but one smectic phase) amyl cyanobenzalaminochinnamate (called for short: cyanobenzal); numerous mixtures of nematic substances with substances having asymmetric molecules.

In substances that present two mesomorphic phases, the phase existing at the lower temperature is always smectic; that which is stable at the higher temperature is either truly nematic or cholesteric. In no case does a same substance (pure or mixed) exhibit a nematic and a cholesteric phase. Therefore, whereas the smectic phase keeps its identity, the nematic and the cholesteric phases mutually replace each other. This is one reason for believing that the cholesteric phase is simply a special form of the nematic phase.

The cholesteric substances may show two distinct structures, so different in aspect that they have often been taken for different phases.

1. *Conic structure.*—This is obtained in general by chilling the isotropic liquid between two perfectly immobilized glasses. With some substances, like cyanobenzal, it undergoes spontaneous change, and becomes an ordered structure. With others it persists, providing the support remains steady, throughout the whole domain of stability of the cholesteric phase. But in general, if the cover glass is shaken, it transforms into an ordered structure.

A remarkable example of this transformation is that of the mixture of azoxyphenetol and cholesterine benzoate. When chilled between two motionless glasses, these mixtures maintain the conic form. If the cover glass be moved ever so slightly everything suddenly changes: The ordered structure appears abruptly and with it the enormous rotatory power and the reflection of magnificent colors. But the points of transformation remain where they are; there is no change of phase, but only a change of structure which brings it nearer to what is observed in the homeotropy of smectic or true nematic substances.

When in the conic form, cholesteric substances appear quite like smectic ones, with the same arrangement of focal conics. But the optical sign is negative without exception, while it is positive in all other mesomorphic substances. There is no trace either of the enormous rotatory power, perceptible in the thickness of a microscope slide, nor is there any reflection of colors.

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* The classification of Lehmann generally adopted in Germany and based on fluidity, combines smectic and the cholesteric substances under the name of Fliessende or Schleimig-flüssige Kristalle, and disposes of true nematic substances under the name of Flüssige Tropfbar-flüssige Kristalle.

2. *Structure of Grandjean's Planes.*—Whether produced spontaneously or as the result of movement impressed upon the cover glass, like the homeotropy of the other mesomorphic substances, ordered structures show the following principal characteristics:

A. *Diffusion of colors.*—The preparation illuminated by ordinary white light diffuses bright colors analogous to those of peacock feathers or Lippmann's photographic plates. Giesel discovered that this colored light is circularly polarized. This divides the cholesteric-like substances into two classes: Dextro-rotary substances, diffusing light circularly polarized to the right (cyanobenzal, cholesterine chloride) and left-handed substances, diffusing light circularly polarized to the left (most of the other cholesterine salts).

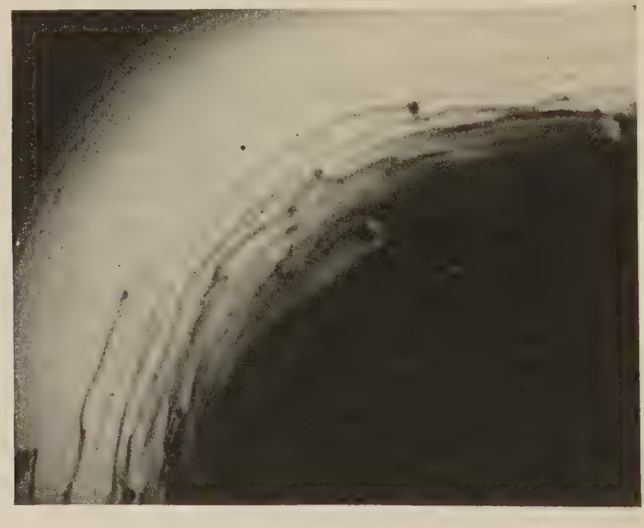

FIG. 14.—Crossed Nichols, × 30. Amyl cyanobenzalaminocinnamate, cholesteric phase, in a crevice of a thin sheet of mica, the Nichols being turned so as to extinguish the mica. "Grandjean's planes" in perfect regularity are seen in thinnest part of the crevice, and become invisible in the thick part, where the structure is disturbed by "oily striæ" (which were displaced in the course of focusing).

The color diffused is not monochromatic but presents a maximum of intensity for a certain wave length L. This wave length L varies according to the two angles made with the normal to the preparation, by the illuminating and the observed rays. It goes from red towards violet in passing from normal incidence to grazing incidence.

B. *Planes of Grandjean.*—The substance appears to be divided in strata by surfaces which in the crack of a thin piece of mica, for example; appear as equidistant planes (Fig. 14). These planes cannot be easily seen, except when they are cut by the faces of an exceedingly sharp prism as in the case of a crack in a cleavage face. As soon as they cut the surface of the preparation at a considerable angle, in the majority of cases they are no longer seen, because they are too close together. Their distance apart is, in the cyanobenzal for example, of the order of 2000 Å. U. and varies with different substances from 1000 to several tens of thousands Å. U. When they are far apart, as, for example, in mixtures of nematic substances and rosin, they are readily visible in all their orientations and even in the conic structure; it is therefore obvious that they play in this structure exactly the same rôle as do the equidistant planes spaced at molecular distances, in smectic substances, and like them they curve in Dupin's cycloids. There is no doubt, therefore, that in the cholesteric substances as in smectic ones, the conic structure is determined by the existence, in the mass of the body, of equidistant surfaces. But while in smectic bodies the distances of these surfaces are of molecular order, some of 44 Å. U. in the alkaline oleates for example, in the cholesteric substances there is stratification at much greater distances apart, approximately several thousands or tens of thousands of Å. U.

The planes of Grandjean show optical properties extremely singular and as yet unexplained. They reflect, nonselectively, one of the circular vibrations, the right in the case of dextro-rotatory substances, the left with the levo-rotatory ones. The other circular vibration traverses them without any modification. Interferences due to equidistance of the planes color the reflected circular light, exactly as in the Lippmann photographic plates. Both qualitatively and quantitatively can thus be explained in a very satisfactory manner the composition of reflected light, according to the variation of incidence. But the cause of the reflection of a circular vibration still eludes us. One is tempted to believe that the planes of Grandjean, which certainly are periodic discontinuities of structure, behave as though they were material having for one of the circular rays a different index from that of the rest of the mass. But this is not the case. The reflection of the circular ray at the planes is, in fact, very different from ordinary reflection. It presents the entirely new characteristic that the right-handed vibration, reflected by the planes of a dextro-rotatory body, remain right handed after reflection. In ordinary reflection the reverse takes place, a right-handed vibration is reflected as left-handed. This is a curious enigma that can be solved only when the structure of cholesteric substances, which is still obscure, is known, as well as the nature of the planes of Grandjean. It is necessary to add that the planes of Grandjean are not the only detail of the visible structure. When the superior surface is free, comma-shaped designs (also discovered by Grandjean) can be seen forming lines between the edges of the planes (Fig. 15). These turn their concavity always in the same way for dextro-rotatory bodies and in a reverse manner for levo-rotatory ones. Under like conditions the intervals between the edges of the planes are each marked with a black fringe visible between Nicols; and, when the preparation is turned, it is displaced in one sense for dextro-rotatory bodies and in reverse sense for levo-rotatory ones (mobile fringes). The existence of these mobile fringes has been completely explained by the discovery of the reflection of the circular ray without change in its direction of rotation.

C. *Rotatory power.*—Finally, when in the plane form, cholesteric substances show an enormous rotatory power, out of all proportion to the rotatory power found elsewhere and reaching as high as *400 turns per millimeter.* This rotatory power bears no relation to the molecular rotatory power of the substance in the amorphous or dissolved form. It bears a direct relation to the plane structure and particularly to the enormous torsion that this structure involves.

The close relation that exists between the rotatory power and the plane structure is demonstrated by the fact that the rotatory power changes in the same sense as the length of the L wave reflected with maximum intensity. When the incidence is varying, if L also varies, the length of the wave of inversion of the rotatory power varies at the same time. This inversion has moreover exactly the same characteristics for all cholesteric substances: Starting with the ultraviolet, the rotatory power, which is right for dextro-rotatory substances and left for the levo-rotatory, diminishes, then presents a minimum from which it increases rapidly towards the length of the L wave. In the vicinity of L, without showing any tendency of diminishing, it ceases to exist in a certain band on both sides of L. From the red side it reappears, changed in its sense of rotation (left for dextro-rotatory bodies, and diminishes rapidly towards the infrared). There are substances for which L is beyond the visible spectrum and which, consequently, do not reflect visible colors.

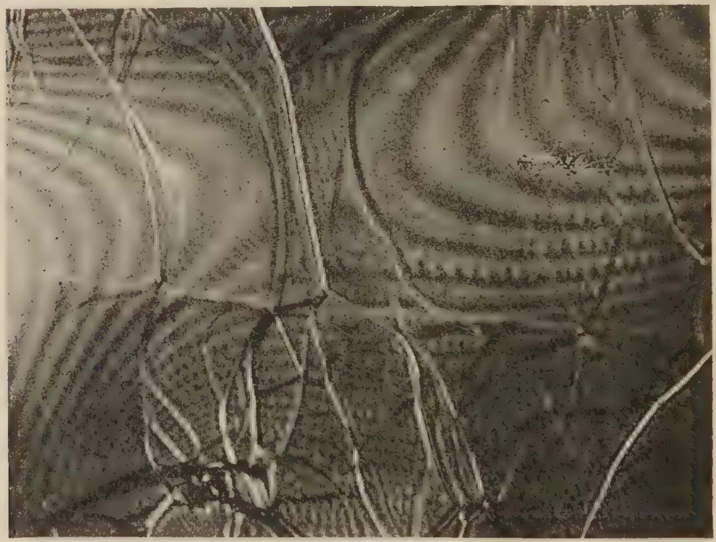

FIG. 15. × 350. Amyl cyanobenzalaminocinnamate, cholesteric phase; very thin layer, melted on a sheet of talc. The specimen is seen through a right-handed circular analyzer, which gives maximum clearness to the mobile fringes and the commas. The borders of Grandjean's planes are not visible under these conditions. There is just one fringe and one line of commas between each pair of planes. Maximum thickness is at the two dark areas where the fringes and the lines of commas are serrated; minimum thickness is at the light areas where the fringes and lines of commas spread apart.

Thus, even though the wave lengths in the neighborhood of L act almost like an absorption-band, neither the rotatory power, the absorption, nor the inversion are in this case molecular phenomena. They are in accord solely with the structure whose essential feature is the existence of the planes of Grandjean, and not with an absorption but with the diffusion of the circular vibration by these planes.

The theory of Mauguin relative to optical properties of the twisted areas of nematic substances makes it evident that when the twisting is very marked, of the order of 100 or 1000 turns per millimeter for example, the properties of these areas will no longer be those that are observed in the slightly twisted areas of true nematic bodies. Therefore a real rotatory power of the ordinary type must appear and this rotatory power, paradoxical as it may seem, must be greater in proportion as the twisting is less. When the twisting diminishes beyond a certain limit the rotatory power, without diminishing its intensity, ceases to manifest itself under the ordinary form, in that the body does not divide the incident vibrations into two circular vibrations but into two elliptical vibrations. When the twisting becomes slight enough, the two vibrations become appreciably rectilinear, and thus we pass to the case of Mauguin's twisted areas. But so long as the rotatory power exists in the simple form, with division of incident light in two visibly circular vibrations, it is greater in proportion as the twisting is weaker.

Now, this is precisely the character that is recognized by the study of mixtures in the rotatory power of the cholesteric substances. On mixing a true nematic substance in decreasing proportions with a substance having rotatory power, for example a cholesteric body, the rotatory power is seen to increase more and more. Without being able as yet to state precisely the details of the plane structure of Grandjean, we are thus led to consider it as involving, in one way or another, extremely powerful torsion, which is stronger when the planes are closer together and which takes place about the normal to these planes. It seems that between plane and plane, the torsion is constant, but it is not yet possible precisely to estimate its value, probably 90°, perhaps twice that.

This torsion which must be left in the dextro substances and right in levo-rotatory ones, while accounting for the rotatory power, also explains the remarkable fact of the negative sign of cholesteric substances.

Under certain exceptional circumstances we can observe a thin layer of a cholesteric substance whose thickness may be materially less than the distance between the planes. In this case the torsion is negligible. The substance then appears to be identical with ordinary nematic substances with a nuclear structure and the true optical sign appears: It is *positive,* as with true nematic substances, and the optical axes are parallel to the plane of the preparation, that is to say, parallel to the planes of Grandjean. It is comprehensible that a torsion about a normal to these planes, while determining the formation of an uniaxial edifice whose optical axis is normal to the planes, at the same time gives rise to a negative edifice, the torsion following a normal to the positive optical axis of the element. It is for this reason that all cholesteric substances, and these only among mesomorphic substances, have a negative sign. In reality the optical sign of the element is positive in all the known mesomorphic bodies.

Study of mixtures has recently entirely confirmed these views. It has shown first that on mixing with a cholesteric substance increasing proportions of an ordinary nematic substance, it acquires gradually, without showing any limit, the properties of true nematic substances.

Extremely small quantities of cholesteric substances (less than one per cent, for example) suffice to maintain the properties as those of the cholesteric type. But even with small proportions, it always ends by passing without discontinuity, from the cholesteric type to a nematic type in which can be observed only Mauguin's areas with weak systematic torsion, and then finally to the simple nematic type. There is nothing like it in mixtures of cholesteric and smectic substances. These two types are always separated by a discontinuity. It is therefore definitely proved that the nematic and cholesteric types are but two aspects of the same type and that Lehmann was wrong when he classed cholesterol with smectic substances. The usual pasty consistency of cholesteric substances, probably a consequence of their twisted structure, is of an altogether secondary character. Besides, X-ray examination is, by itself alone, convincing: Like nematic substances, cholesteric substances do not diffract X-rays. The wave lengths of the visible spectrum alone are diffracted. Between their stratification and that of smectic substances there is the same difference in order of size that there is between the wave lengths of X-ray and those of the visible spectrum. As molecular structures, they do not differ from nematic substances.

Mixtures of a dextro substance (cyanobenzal) and of a levo substance (cholesterine benzoate) are also very instructive. They have allowed us, so to say, to untwist a cholesteric substance and to prove that it then becomes an ordinary nematic substance. For each proportion of this mixture there is a temperature T for which the mixture, dextro-rotatory below T, becomes levo-rotatory above. The temperature T is higher in proportion as the percentage of the dextro-rotatory substance is greater. Between two determined limits (2.25 to 3 parts of cyanobenzal to 1 of benzoate) the temperature T is included within the interval of stability of the cholesteric phase. For a mixture of 2.5 or 2.75 parts of cyanobenzal and 1 of benzoate, on increasing the temperature, a cholesteric dextro-rotatory substance is first seen. Then as T is approached Grandjean's planes gradually spread apart, and the commas disappear. When the temperature T is reached, the planes have disappeared, as have also the commas and the movable fringes and there is no longer any rotatory power: The substance has become a simple nematic body in which the *positive* optical axes are parallel to the plane of the preparation. But as soon as the temperature T is exceeded, the planes reappear, also the commas, the movable fringes and the rotatory power; and the planes now reflect the left vibration, the commas and the movable fringes take the characters that they have in levo substances—the rotatory power has changed its direction. The dextro substance has become levo-rotatory. It seems therefore very clear that between dextro and levo substances there is but a difference in the direction of twisting and that cholesteric substances when thus untwisted at the point T, are simply of the true nematic type.

To sum up this very incomplete examination of the properties of the mesomorphic forms, there is added a table of the states of the organization of matter in the order of increasing temperature (or dilution).

1. *Crystalline State.* (One or many, separated by discontinuities.)
   Discontinuity T_1.

Mesomorphous States

2. *Smectic State.* (Sign +)
   Discontinuity T_2.
3. *Nematic State.*
   A. *True nematic state.* No rotatory power. Sign +.
   B. *Cholesteric state.* Rotatory power. Apparent sign —.
      a. *Dextro-rotatory.* Right-handed twisting. Reflection of the right-handed circular ray.
      b. *Levo-rotatory.* Left-handed twisting. Reflection of the left-handed ray.
   Discontinuity T_3.
4. *Amorphous State.*

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Colloids as One Phase Systems

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Van't Hoff once expressed the opinion that the word "phase" was used far too extensively; it became a habit, he said, to speak of a liquid phase, a solid phase, where one might have employed just as well the expression a liquid or a solid substance.

Similarly, it appears, the word phase is nowadays abused in colloid chemistry, and the impression is given that the notion phase might be of outstanding importance in this branch of science. I propose to show in this article that such is not the case, since it proves impossible to make out whether a colloid is composed of one or two phases: in fact, both conceptions are equally justified and no conclusive reasons have ever been given in favor of either of them.

The most characteristic point of the phase doctrine is that it enables us to classify every system of substances according to the number of components and phases, and to draw the limits of the fields of existence of the different phase complexes. The last problem, however, very seldom appears in colloid chemistry, since new phases only rarely arise. The freezing of sols and gels, and the equilibrium of hydrogels with water vapor may be given as examples. Therefore, the application of the phase rule proper will be of value in a few cases only. As to the first question, the classification of systems, it is clear that the number of phases constitutes the ruling factor and, therefore, must be unequivocally defined before going further.

It is quite generally assumed that in sols and gels two phases must be distinguished, whereas only a few authors contend that they may be considered as one phase systems. It appears, however, that the first supposition has been reached rather by generalization and extrapolation than on substantial grounds. The supporters of this conception argue as follows: Sand and water form two phases, since they are mechanically separable, *e.g.*, by filtration. If we grind the sand to a finer powder, we do not detect any point where the number of phases would suddenly be diminished by one. If we take a substance like barium sulfate, which may be obtained in still smaller particles, we find that it goes through the filter, that it does not settle to the bottom, etc. The barium sulfate and the water now seem to be mechanically inseparable, but on closer inspection, we find that by taking filters with smaller pores, by using centrifugal force, etc., the two substances may, however, be separated. Thus, in this case too, we may speak of two phases. Again, since these systems diffract the light and are therefore optically inhomogeneous, the broad generalization was reached that all systems with the same property were to be considered as two phase systems.* In order to examine whether this conclusion is justified, it will be necessary to analyze first of all the meaning of the notion "phase."

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* We shall see later on that some authors (Bary, for instance) have more or less definitely receded from this opinion for a part of the colloid systems.

The Concept "Phase"

The most important point in the above reasoning is heterogeneity: in fact, we find many authors stating that a system consists of two phases, because it is heterogeneous.[1] Here confusion arose; it might have been avoided if one had generally realized that the word heterogeneous has only a relative and not an absolute meaning. In the definition of the idea *phase*, it has therefore to be taken in a relative sense, as has been already clearly explained by Bakhuis Roozeboom [2] and Perrin.[3] The founder of the phase notion, Gibbs, wrote: [4] "in considering the different homogeneous bodies which can be formed of any set of component substances, it will be convenient to have a term which shall refer solely to the composition and thermodynamic state of any such body without regard to its quantity or form. We may call such bodies as differ in composition or state, phases. (By homogeneous is meant that the part in question is uniform throughout, in chemical and physical state.[5])" Thus, a phase is a part of a system, in which definite values may be assigned to the variables determining the state of the system, as pressure, temperature, concentration.[6] This can only be done, if such a phase contains a very great number of molecules, either at one moment or within a very short time, and if the velocities of these molecules are distributed according to Maxwell's law. Of course these definitions are entirely thermodynamical and for practical use other ones have been introduced. Wilhelm Ostwald [7] and Findlay [8] consider phases to be different portions of a system, each in itself homogeneous, but marked off in space and separated from the other portions by bounding surfaces. It is significant that both authors felt the need of adding the last phrase, to which Findlay joins in addition the words "mechanically separable." They clearly intended to give the name *phase* only to parts of certain dimensions and to exclude the possibility of considering one molecule as a phase.

Bakhuis Roozeboom gives the definitions: phases are the different modes of appearance, each in itself homogeneous, exhibited by a number of substances which are brought together. Perrin writes: "if two regions in space are filled with a homogeneous substance, which is identical for both volumes, these masses of matter are said to belong to the same phase." So, these authors too state explicitly that a phase should be hemogeneous, but preceding remarks on the significance of this expression contain the clue to the problem. Homogeneity is only possible, says Roozeboom, on account of the smallness of the molecules and the roughness of our methods of observation. Every time we make use of the molecular theory, declares Perrin, we admit that no rigorously homogeneous substance exists. Strictly speaking, we should have to consider a sugar solution or even the air as heterogeneous and as a two phase system, since it would be possible to indicate very small parts of space, which would contain only water and only sugar molecules, or only nitrogen or oxygen molecules. Therefore we must realize that a system may be at the same time homogeneous and heterogeneous according to the standpoint that we take.* If we can divide a certain volume of a solution in small parts which are all alike, we may call and do call the solution homogeneous, even though the parts themselves are not homogeneous. In the same manner we may deal with a quantity of water, in which some oil has been dispersed into small drops, having a diameter of, say, one micron and remaining at a distance of one μ from each other. If we divide this emulsion into cubes having a length of two μ, every cube will contain one oil drop surrounded by water molecules. All cubes will be identical; the emulsion may be called homogeneous, but the cubes themselves may not. One may, on the other hand, imagine a glass of water with only one oil drop floating in it: this system will necessarily be heterogeneous, because it can be divided only into non-identical parts. Therefore, if only the different identical parts into which the system may be divided are sufficiently numerous, the system may be considered as homogeneous; in many cases it must be, if we are not to fall into inextricable difficulties. Even when we take thousands of glass bulbs and have them floating in a large basin filled with a liquid, the whole might be taken for a homogeneous system by giants who would not be able to discern at once the difference of various parts and to observe the dimensions of the bulbs.

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* Zsigmondy also stressed this view. See "Colloids and the Ultramicroscope" ("Zur Erkenntnis der Kolloide"). J. A.

We might introduce, as Bredig has proposed, the expression microheterogeneous, meaning thereby that the dimensions of the different parts are very small with regard to those of the system as a whole; but not much will be gained by doing so.

Returning to our starting point, we conclude that when defining the word phase, homogeneous must be taken in the relative and not in the absolute sense, as the majority of colloid chemists seem to think. An emulsion of oil in water may be considered as one phase, although it is strictly speaking heterogeneous. *A fortiori* a colloid, like egg white or gold sol or a gelatin jelly, may be regarded as forming one phase.

The general acceptation of the belief, that a system consists of two phases because it is heterogeneous, is all the more surprising, since we know of two other cases, in which a heterogeneous system is regarded as composed of one phase only. In the first place, the critical phase may be mentioned which arises on heating a liquid in a closed tube—or two only partially miscible liquids—until the meniscus disappears; it is characterized by a more or less marked blueish opalescence, which is observable until a few degrees above the critical temperature. This opalescence indicates doubtless an optical heterogeneity, due to the fact that the molecules are not uniformly distributed. As Kamerlingh Onnes, Keesom, von Smoluchowski, Einstein,* and others have shown, there occur in this state accumulations and rarefactions of molecules, varying according to time and space, and leading to the temporary formation of tiny volumes of greater or smaller density. These volumes, which are even to be found in ordinary gases, are in the critical phase sufficiently large, and contain a sufficient number of molecules to cause a visible heterogeneity. Although the system is therefore certainly heterogeneous in the absolute sense, nobody has thought of considering it as consisting of two phases.[9] In the second place, attention may be drawn to the liquid crystals. It is well known that these are partly turbid liquids and that Tammann on this account thought them to be emulsions. De Kock, Miss Prins, Treub, however, proved beyond doubt that they consist of one phase only. These authors, in fact, showed that liquid crystals form mixed crystals with each other and with normal solid substances; all systems behave with regard to the phase rule exactly so as ordinary mixed crystals and are therefore one phase systems. Friedel,[10] † who calls them mesomorphic states, also adheres to this view. Nevertheless, their turbidity shows them to be heterogeneous. So we find another instance of systems, which are at the same time heterogeneous and one phase; the explanation of the turbidity is given by Friedel, who shows it to be due to the birefringence in connection with the rapid variation of the optical orientation from one point to the other.[11] All this only corroborates our opinion that strictly heterogeneous systems, like emulsions, colloids, etc., may without difficulty be considered as one phase systems.

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* See paper by A. Einstein, this volume. J. A.
† See paper by G. Friedel, this volume. J. A.

ARE THERE CONCLUSIVE ARGUMENTS IN FAVOR OF THE TWO PHASE THEORY?

Apart from the heterogeneity, dealt with in the preceding section, several arguments have been thought to prove the two phase theory; we shall now consider them in some detail.

Bütschli[12] was the first to investigate the structure of a gel under the microscope and concluded from his observations that two phases were seen. However, the structure was at the very limit of visibility and could only be obtained by the use of special methods (*e.g.*, the addition of alcohol or chromic acid), whereby the original substance is quite markedly altered as is already seen upon superficial inspection.* Bütschli's observations are, therefore, of no value for the problem of the original colloid. Moreover, Zsigmondy and Bachmann[13] have shown the true structure of the pure hydrogel to be much finer and observable only with the aid of the ultramicroscope. Even when using this instrument they found it impossible to resolve more concentrated jellies and they were only able to establish an amicroscopic discontinuity by the observation of the Tyndall phenomenon. As we have seen, optical heterogeneity does not prove a system to be a two phase one, the Tyndall phenomenon even occurring in sugar and other undoubtedly molecular solutions, if only the intensity of the incident light is sufficiently increased.[14]

Sir W. B. Hardy[15] has observed the separation of small drops when a warm mixture of gelatin, water and alcohol is cooled under the microscope. The same remark as above may be raised against this experiment, viz., alcohol changes the properties of the gelatin thoroughly. The argument is, however, completely invalidated when we consider the possibility of separating a mixture of alcohol and water into two layers by the addition of different salts, *e.g.*, potassium carbonate.[16] Here, too, drops will be seen in the beginning, but nobody will consider the alcohol and water mixture a two phase system.

Another experiment also made by Hardy is the following: If an agar agar jelly is compressed within a cloth, liquid is squeezed out. Hardy assumed the liquid, which contained a little agar, to be one of the two phases of the jelly, whereas the mass remaining in the cloth and composed of a more concentrated agar solution forms the second phase. This hypothesis, however, is unproved, since no reason is given why water cannot be pressed out of the second phase also. The phenomenon may be as well taken as an analog of the osmotic experiment, in which a higher pressure than the osmotic pressure is exerted on a sugar solution contained in a porous pot with a semipermeable membrane; water is, then, squeezed out in exactly the same way as in Hardy's experiment. The only difference lies in the nature of the semipermeable membrane: in the case of agar, the cloth acts as such. As in many other cases it does not work perfectly, but allows a little agar to pass; this is why Hardy finds the liquid pressed out contains some agar. These experiments therefore do not give conclusive evidence either. It may be remembered that Bancroft,[17] too, denies their demonstrative cogency.

* Artefacts of this kind are what the microscope shows mainly, in "stained specimens, where the original structure is wrecked by methods which Bechhold characterizes as "cooking recipes." The use of the dark field on untreated material often reveals unsuspected conditions and facts. J. A.

The fact that the diffusion velocity of salts in jellies is nearly the same as in water, has also been advanced as a proof for the two phase theory. However, this approximate equality holds only for jellies that are not too concentrated and for the chlorides of a great many metals;[18] on the contrary, sulfates, acids and bases diffuse in jellies much slower than in water. It is clear, then, that we cannot explain this behavior in a simple way and content ourselves by assuming that the diffusing salt moves through the water phase only. There are two possibilities: either the jelly substance, say gelatin, forms thin walls across the path of the salt, whereby its diffusion will be hindered, or the gelatin particles are uniformly distributed in the liquid like an ordinary solute. On the first alternative all salts should exhibit a diminished diffusion velocity, on the second one there should be no change, unless when a specific action between gelatin and salt takes place, whereby it would be possible to account for the different behavior shown by various salts.

One more argument has been adduced by Martin H. Fischer,[19] who measured the electrical resistance of gelatin-water mixtures at different temperatures and found that it increased on cooling. Especially in the region where the sol gelatinizes, the resistance increases very sharply. As the same phenomenon was detected on cooling a solution of phenol in water,[20] Fischer concluded that both systems are comparable and that the increase of resistance in both systems is to be ascribed to the same cause, viz., the appearance of a new phase.* Apart from the very peculiar theory which he develops for the phenol-water system, which is not likely to meet the assent of physical chemists in general, it is clear that such far-reaching conclusions never may be drawn from an agreement like this, which might be explained in so many other ways.

Difficulties of the Two Phase Theory

If we accept the two phase theory, we have to take in account the surface tension which shows itself in every interface. Different opinions with regard to it have been expressed, which will be dealt with in the following in connection with the question how to apply the phase rule in colloid chemistry. This has been a special subject of investigation.[21] Since, according to Gibbs, the ordinary phase rule only holds so long as the phases are present in large masses, it seems that the rule needs to be altered, if it is to be used in colloidal systems. The number of variables increases by one or two; in the first place, by the specific phase surface, $\frac{\text{surface}}{\text{mass}}$[22] or $\frac{\text{surface}}{\text{volume}}$,[23] or by the degree of dispersity $\frac{ds}{dv}$ (s surface, v volume),[24] in the second place by a magnitude of the nature of a concentration, and defined either as: mass of the dispersed phase divided by mass of the dispersion medium, or as: the number of dispersed particles per c.c. Both definitions come to the same thing, viz., the proportion of the quantities of the two phases.

This variable has been rightly introduced by Pawlaw and Tollman to account for the fact that the properties of a colloid like gelatin (for instance the vapor pressure) are considerably changed on adding or withdrawing a certain quantity of water, in complete contradiction to the behavior of an ordinary two phase system, *e.g.*, phenol-water, in which the addition of one of the components alters only the quantity of both phases, but does not affect their compositions nor the equilibrium of the system. The conflict is particularly striking for those who lay stress on Hardy's experiments with agar; they are obliged to admit that the composition of the two phases of an agar jelly varies according to the quantity of agar in the gel. It is clear, then, that in order to avoid violation of a fundamental principle of the phase rule, one more variable has to be introduced, whereby the number of degrees of freedom is also increased.[25]

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* See paper by M. H. Fischer, Volume II of this series. J. A.

With regard to the first extra variable mentioned above, it may be shown along different lines that it can be dispensed with in the equilibrium state. Then, Jonker remarks, the surface tension has a fixed value, implicitly given by the equations for the thermodynamic potentials; therefore it does not constitute an independent variable. The problem has been more lucidly treated by Tolman. In agreement with others, this investigator argues that a dispersed system can never be in equilibrium, since there will always be a tendency to diminish the surface; the equilibrium state would, therefore, be one big drop floating in the dispersion medium. One exception, however, is admitted. If all drops or particles were of the same size, we would have an equilibrium state, although a metastable one, as any particle accidentally larger than the others would grow at the expense of the rest. This, of course, is quite true, but it seems to lead to a still farther reaching conclusion, namely that the equilibrium is even labile and that, therefore, such states never persist.

If we do not take the view that all colloidal systems are in a state of permanent evolution and never in equilibrium, a view to which the stability of so many sols is in apparent contradiction, we may resort to another explanation. As is well known, colloidal particles carry an electrical charge. Now, Sir J. J. Thomson [26] has already proved that this charge will tend to increase the surface, thus counteracting the effect of the ordinary surface tension; it may happen that for a certain size of the particles the resultant tension is zero.* If we assume that this point is reached in the stable sols, we see that these are in permanent equilibrium: they consist of particles all of equal size, but electrically charged. We arrive in this way at the same conclusion as above, namely that the surface tension in the equilibrium state does not need to be taken into consideration. Only one extra variable therefore remains and consequently the phase rule takes the form $F = n + 3 - p$.

Practically this leads to the same result as when we consider the colloid one phase and take only the normal variables, since in this case the rule holds $F = n + 2 - p$, in which p is smaller by one than p in the first formula. So, the study of the equilibrium conditions will not enable us to decide upon the number of the phases in a colloidal system. The introduction, then, of a new variable and a modified phase rule seems to be an unnecessary complication, due to the assumption of two phases.

Positive evidence against the two phase theory has been adduced by Hatschek,[27] who calculated, on certain theoretical suppositions as to the polyhedral structure of a gel, the elongation caused in it by a known stress. When comparing the values obtained with those found experimentally by Bjerkens for gelatin and for rubber, complete disagreement appears. As no other physical structure than the one assumed seems possible, Hatschek declares that the two phase theory must be rejected.

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* For lyophilic colloids in which the electric charge does not seem to be absolutely necessary, Tolman assumes a negative tension which also would take the value zero at a fixed degree of dispersity. This force, however, could in my opinion lead only to complete disaggregation, *i.e.*, molecular dispersion.

More difficulties arise, when we follow this conception to its consequences. Let us consider, for instance, Spiro's observation[28] that, if we add sodium sulfate to a casein sol, two liquid layers are formed, each containing water, sulfate and casein. Reasoning consistently, we must assume this system to be composed of four, in any event three phases, instead of two, since both casein-containing liquids, or at least the casein-rich one, are to be counted as two. Many instances like this may be given; we only recall the agar gel, dealt with before, which was divided seemingly into two phases, but in reality—from the standpoint of the supporters of the two phase theory—into three or four. Again, the three component system tannin-water-ether may be considered.[29] A solution of tannin in water behaves itself as a colloid, whereas tannin dissolves in ether as a crystalloid. If we add some ether to the tannin-water mixture, which is to be regarded as a two phase system, a turbidity arises and on standing three liquid layers are formed. Jonker, as every one would do on first sight, has counted these as three phases; but if we consider the original sol as two phases, it appears only logical to consider the three layers as four or five phases, the third one being an ordinary solution of tannin in water with only a little ether.

The ultimate conclusion to which the two phase theory leads, would be, that we should consider even an ordinary solution as two phases. As we never detect any abrupt change, as the characteristics of the colloid systems (Brownian movement, diffusibility, osmotic pressure, etc.) gradually vary and approach those of ordinary solutions,* there is no possibility of avoiding this unpleasant consequence,† by which Gibbs' fruitful distinction between phase and component would be completely abolished. The view has been defended, indeed, by some authors many years since, but few will agree. It makes a renewed consideration of the problem desirable, in order to see if there is some means of escape.

THE ONE PHASE THEORY

We reach the one phase conception, when starting from a sugar solution which is generally regarded as one phase, doubtless in agreement with Gibbs' meaning. If we replace the sugar by some organic dye-stuff with a much higher molecular weight, we notice only a gradual change in the typical properties of the solution; for the same concentration by weight we find lower osmotic pressure, we observe smaller diffusion velocity, etc. Taking substances with increasing molecular weight, like albumin, hemoglobin, or rubber, and placing them in water or benzene, we continue to observe exactly the same phenomenon: the solid substance dissolves spontaneously, the osmotic pressure falls again and the diffusion velocity decreases. It has been shown by Hüfner[30] and Zsigmondy[31] that the osmotic pressure law still holds for hemoglobin as for a gold sol, for the molecular weights of these substances (by this expression is meant the weight of the individually moving particles) calculated from the osmotic pressure in the ordinary manner, agree with data obtained from other experiments. When, now, we find that a solution of another similar substance fails to exhibit as small an osmotic pressure or as slow a diffusion velocity, we shall obviously prefer to claim that these quantities have fallen to experimentally unmeasurable values instead of assuming that these quantities are absolutely zero. In other words, we had better consider the systems involved as solutions with very heavy molecules and, therefore, as one phase systems, than to call upon some mysterious force, which suddenly gives rise to a new phase, the appearance of which cannot be deduced from any phenomenon.

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* Even the mechanical separability persists; the reverse of osmosis—the pressing out of liquid through a semipermeable membrane, when a pressure is applied higher than the osmotic pressure—is theoretically nothing else than filtration of molecules; it is connected with ordinary filtration through the intermediate process, known as ultrafiltration. Dialysis also is no longer a means of distinction between sols and solutions, since collodion membranes can be made of ever decreasing pore size. [See paper on ultrafiltration by H. Bechhold, this volume. J. A.]

† Sea water would form a system of a great many phases, air at least one of five, etc.

In a preceding section enough has been said to show that the absolute heterogeneity of such systems does not constitute a difficulty to regarding them as one phase systems.

Another objection raised is this: it is not permissible to speak of molecules and molecular weights, because other notions are indicated by these terms, and because it is impossible to indicate a definite weight, the particles of colloids never being of one size. Although it is quite clear, what we mean by molecule and molecular weight in colloid solutions (namely, the isolated particles), it might indeed be preferable to use in this case the expression micell and micellar weight, the latter being determined in exactly the same way as the molecular weight in ordinary solutions. The fact that the micells have different weight does not cause any trouble, for we find in normal solutions analogous phenomena. Indeed, we use always average molecular weights, which in many cases may surely be taken as the real weights of the isolated molecules, but which in as many other instances are not, for example, in solutions of electrolytes, of acetic acid in benzene, or in the vapors of sulfur and hydrofluoric acid.* In all these examples we assume the solute or the vapor to consist of various molecules and their polymers, the composition and number of which are only hypothetically known. Exactly in the same way the phenomenon in colloids may be interpreted. No more value is to be attached to the remark that the particles or micells do not comprise only one component, but contain also water or solvent in general. In fact, many investigators assume that in ordinary solutions the molecules or ions of the solute have combined with solvent molecules and this does not prevent them from determining the molecular weight. So, this too cannot be regarded as an objection to the thesis that colloids and ordinary solutions are completely analogous and both one phase systems.

As to the positive evidence for this conception, it is obvious that all difficulties met with in the two phase theory are just so many arguments in favor of the one phase theory. We need only point to the application of the phase rule and the superfluity of introducing a new variable. The concentration of the dispersed phase is, in fact, nothing else than the concentration of one of the components; the surface tension which for lyophile colloids was taken as negative by Tolman, does not need to be considered. It is the same force that causes any substance to dissolve. We do not need to make a distinction between colloids with a positive and with a negative surface tension; in both classes, when equilibrium is reached, the tension is zero, but for different reasons.

The one phase conception has been used consciously by investigators like Katz, Sörensen and myself,[32] whereas it is assumed without explicit statement in researches by Perrin, von Smoluchowski, Loeb.

With great success Katz[33] applied it in his extensive and penetrating investigations on swelling. He was thereby enabled to explain the behavior of swelling gels as completely analogous to that of an ordinary solution. He proved, for instance, that if we determine the vapor pressure of a swelling gel as a function of the water content, the same curve is found as if we had taken sulfuric acid or glycerin instead of gelatin or starch. He showed that the heat of swelling corresponds to the heat of mixing or solution, as the swelling pressure to the osmotic pressure. Relations between several of these magnitudes were deduced and were shown to be in agreement with the experimental results. Swelling gels, in short, behave as ideal concentrated solutions, the theory of which had been given by Nernst. Perhaps no better plea for the one phase theory can be adduced.

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* See paper on Molecular Aggregation by W. E. S. Turner, this volume. J. A.

Galeotti [34] and Sörensen also regard albumin solutions as one phase. Dealing with the separation of egg white from its aqueous solution by saturation with ammonium sulphate, Sörensen proved the phase rule to hold.[35] As this rule required, the egg white concentration in the sol was constant, so long as the egg white was present in the solid state, in other words, as a new phase. Particularities, it is true, were observed, because the equilibria established themselves only very slowly * and depended greatly on small quantities of impurities; but the principle of applying the phase rule and considering the albumin solution as a one phase system is not thereby invalidated.

Perrin, in his famous research on the distribution of gamboge particles with height in water, speaks of the osmotic pressure of these particles; the author tacitly assumes that he is dealing with one phase. The same is done by von Smoluchowski,[36] when he treats the kinetics of coagulation in a like manner as a reaction velocity and declares, that coagulation and chemical reactions are opposed extreme cases, between which probably transitional processes will exist; a treatment which leads to results agreeing with the experimental data of several investigators.

Again, Loeb may be mentioned, who in his treatise on the proteins and the theory of colloidal behavior successfully regards colloid systems as one phase.

Finally a very recent paper [37] of Miss Laing's adduces new evidence. As the result of an exhaustive study of sodium oleate solutions, she concludes that electrolytic migration and electrophoresis are strictly identical, both phenomena being governed by the same law. This is exactly what the one phase theory predicts; between the electrolytic conductivity and the electrophoresis there is only a quantitative difference, the number of carriers of electricity being in the first case enormously greater than in the second. In connection herewith attention may be directed to the possibility of extending Debye's new theory of strong electrolytes, with its conception of ionic atmospheres, to the colloidal solutions.

It is no wonder that all these considerations have caused some partisans of the two phase theory to waver. So Bary [38] expresses the opinion that stable suspensions, as he calls what is generally designed by lyophile colloids, should be regarded as one phase systems, whereas unstable suspensions, or lyophobe colloids, should be considered two phase systems. The distinction between these two classes would depend on the sign of the surface tension; [39] if it is positive, we should obtain two phases; if it is negative, only one. We might also say: if the colloid spontaneously dissolves, we regard the liquid as one phase; if it is to be brought into solution with the help of any external agency, we consider the liquid as two phases. Remembering, however, the considerations previously given on the value of the surface tension as a result of counteracting mechanical and electric forces, we see that Bary's distinction

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* In fact, this peculiarity is also exhibited by many ordinary equilibria, for instance, those of the hydrates of thorium and cerium sulfate.

cannot be maintained. Moreover, it obviously brings us into great difficulty, when we take the case of a common gold sol to which some protective colloid is added. According to Bary the gold sol initially consists of two phases, since it is unstable. But as soon as some gelatin is added, Bary must from his point of view regard the sol as one phase, since the gold now, when obtained in the solid form by evaporating the sol, redissolves spontaneously in water. It is, of course, not clear why the sol, without change in its appearance, should suddenly pass from one state to the other.

Even Freundlich seems to approach to the same view as Bary's. At least, he declares that much is to be said in favor of the opinion, that the separation of the dispersed phase of a lyophile sol is the same phenomenon as the separation of a sparingly soluble substance, for which the phase rule holds;[40] and he writes, a few pages[41] further on, that one should be careful with the statement that lyophile sols behave fundamentally in a different fashion than true solutions.

Conclusion

The preceding demonstration will have made it clear that both theories are equally acceptable. No cogent reasons have been found whereby either of them could be proved, either for all colloid systems or for a certain group. We therefore cannot declare a colloid to be a one or to be a two phase system; we ought to say, it is both. How we shall regard it in any given case, depends on the kind of problem we are investigating. We must in each case choose the most appropriate conception. It is certainly not useful, though theoretically possible, to treat coarse suspensions as one phase systems, nor is it suitable either to consider egg white or rubber solutions as two phase systems. As to this choice, it is a significant fact that the partisans of the one phase theory have mostly entered the field of colloid chemistry from the biological side (Pauli, Sörensen, Loeb) or have considered it from a general thermodynamical point of view, whereas the defendants of the two phase conception have started from the study of capillarity and adsorption (Freundlich).

The controversy between both theories is, therefore, solved in the same manner as the question, keenly discussed twenty years ago, whether the colloids were solutions or suspensions. Like this, it turns out to be a senseless conflict. This being so, it would be better to banish the word phase altogether from colloid chemistry and to accept von Weimarn's proposal,[42] to replace it by "part" and to speak of the dispersed part instead of the dispersed phase.*

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* W. D. Harkins calls them "regions." See his paper, this volume. J. A.

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22. Pawlow, *loc. cit.*

23. Wo. Ostwald, *Grundriss der Kolloidchemie,* § 5.

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39. Compare Tolman's article previously cited, in which he, too, draws a line between these two groups according to the same principle.

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The States of Matter Exemplified by a Typical Colloid. Soap and the Soap Boiling Processes

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The oils and fats used in soap manufacture are mixtures of such numerous substances, and the forms which soap can take afford such striking diversity of properties and behavior, that it would at first sight seem impossible to attempt a description which would be at once simple and exact. However, it is a remarkable discovery that a simple two-component system consisting of water and any sodium or potassium salt of any higher fatty acid exemplifies all of the forms which a mixed soap assumes.

There is a strong resemblance in type between all the members of the large family of the sodium and potassium salts of the fatty acids—they differ in degree rather than in kind. Furthermore, the action of various electrolytes upon them, is very similar so that by the use of constant numerical factors, the behavior of any mixture of salts can be inferred from that of one typical salt.

Throughout the soap boiling operations, which involve such complicated mixtures, there is no separation or fractionation of the various constituent soaps except during crystallization. Hence, almost the whole of the behavior of any mixture of soaps and electrolytes can be exemplified by considering the simple three-component system water, pure salt and any pure sodium or potassium salt of a fatty acid. It is easy then to proceed to the discussion of the modifications due to fractional crystallization.

Our first and chief task is to characterize the various forms which any aqueous solution of a pure soap can assume and to examine the conditions under which each appears. Soap solutions are excellent examples of reversible colloids and it has been found by McBain and Burnett[1] that for purposes of the phase rule a solution of reversible colloid, no matter how complicated in itself, behaves towards external equilibria as a single phase. Hence, it does not affect the simple behavior required by the phase rule that soap solutions are colloidal electrolytes[2] in which there are in equilibrium crystalloidal and colloidal constituents ionized and un-ionized.

Any soap mixed with water in various proportions and under suitable conditions, can be made to assume any one of five different forms, all of which behave as single phases from the standpoint of the phase rule. Many soap solutions can also be made to gelatinize, but it will be seen that this does not constitute formation of a new phase. Of these five forms, two are crystalline, two are liquid crystals or anisotropic (doubly refracting liquids) and one is a range of solutions which extends all the way from crystalloidal to colloidal but which are ordinary isotropic or singly refracting solutions. Each of these forms will now be briefly discussed.

(1) *Lamellar Crystals of Soap.*—The pure anhydrous salts of the fatty acids never occur in commercial soaps, but the more varied experimentation possible in the laboratory shows that this is due merely to the usual soap boiling procedure. The anhydrous soaps, when pure, are colorless powders at room temperature, but on heating to about 200° C. they melt to form typical liquid crystals and at about 300° C. these suddenly turn to a mobile isotropic liquid which is miscible with water in all proportions (necessarily under pressure at such high temperatures). At less elevated temperatures, when soaps crystallize out from aqueous solution, they may form very thin lamellar crystals which consist of hydrated soap. These are more characteristic of potassium soaps than of sodium soaps and are familiar in the "figging" of soft soaps. The lamellar crystals frequently have sharp edges and Mr. S. H. Piper [3] has shown by X-ray examination that they are typical crystals yielding radiographs with numerous fine lines. Every potassium or sodium soap can crystallize either in this lamellar form or as curd fibers.

(2) *The Curd Fibers of Soap Curd.*—It is a commentary upon the present state of our science that different investigators at the present time hold such irreconcilable opinions with regard to the nature of soap curd. Martin H. Fischer,[4] under the influence of Wo. Ostwald's conception of emulsoids, regards curds as jellies in which soap is the continuous phase in which the aqueous solution is dispersed. Friedel,[5] in order to include amongst liquid crystals such bodies as soap curds, has gone so far as to reclassify and rename the groups of anisotropic liquids (liquid crystals). For this purpose he assumes that soap curds are homogeneous single phases, doubly refracting with the molecules arranged on equidistant surfaces like a collection of superimposed monomolecular films; nothing is said as to the whereabouts of the water. Merklen,[6] attempting to apply the earlier colloidal conceptions, assumed that commercial soaps were "sorption compounds"; whereas Lewkowitsch,[7] impressed by their constancy of composition in commercial practice, maintained, like Chevreul, that they were to be regarded as compounds containing "water of constitution." A number of scientists would regard soap curds as gels or even jellies with water as the continuous phase, whereas the writer [8] has concluded that soap curd consists of a soap solution which has partially or wholly crystallized out in the form of innumerable curd fibers which naturally enmesh the remaining mother liquor or soap solution. This is also the standpoint taken by von Weimarn [9] in his criticism of Zsigmondy and Bachmann's paper.

The criteria upon which the writer relies are as follows:

(a) Not only can the curd fibers be seen under the ultramicroscope, but the individual fibers can be manipulated and disentangled by hand. Beautiful photographs have been published by Zsigmondy and Bachmann [10] and by McBain, Darke and Salmon.[11]

(b) Whereas all transparent soap solutions whether fluid, gelatinous or plastic, isotropic or anisotropic, behave like concentrated solutions, that is, they have high conductivity and osmotic properties, these opaque white soap curds show, through all these properties, that the soap has been almost completely removed from solution. This is confirmed by analysis of the mother liquor which is very readily squeezed out. The suddenness with which curd appears on cooling accounts for the sudden diminution of conductivity which Fischer ascribes to reversal of phases.*

(c) X-ray photographs of soap curds obtained by Mr. S. H. Piper [3] are of exactly the same type as those obtained from ordinary crystalline fatty acids which are now universally admitted to be truly crystalline.

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* A paper by M. H. Fischer will appear in Vol. II of this series. J. A.

(d) Soap jellies which are perfectly transparent and which exactly resemble gelatin jellies occur, but in dilutions in which, through heating or addition of water or through supersaturation, curd fibers are completely absent. Such true jellies exhibit the high conductivity and osmotic activity characteristic of colloidal electrolytes. Like gelatin jellies they are not liquid crystals, but are isotropic and they do not give a radiograph.

(3) *"Neat Soap."*—"Neat soap" is the name given by the soap boiler to the upper liquid layer of concentrated soap which merely has to be cooled and cut into bars or stamped to serve as household or bar soap or be utilized as "base" for the production of toilet soaps. Under such conditions its composition is remarkably constant, seldom falling appreciably below 63 to 64 per cent of fatty anhydride or 69 to 70 per cent of anhydrous sodium soap.* It of course alters in structure and physical characteristics on cooling, becoming soap curd, owing to crystallization of the least soluble soaps as curd fibers.

It will now be shown that the soap boiler's "neat soap" is but a particular case of a form of soap which can exist over a wide range of concentrations and temperatures and the term "neat soap" will be used to describe the whole of this state. "Neat soap" is a liquid crystal, that is, a doubly refracting, plastic liquid. It is clear and transparent; though often colored, no discontinuities are visible and a layer in which the liquid crystal has the same orientation throughout, causes no distortion of objects seen through it. There are no particles or fibers to be seen in it and the microscope shows that it is quite continuous so that the turbidity often exhibited when the specimen has been stirred, is seen by examination under crossed nicols to be caused by different orientation of the doubly refracting liquid in different portions of the same mass. In other words neat soap is a single homogeneous phase of the same composition and structure throughout. This is in great contrast to the curd which the ultramicroscope and often even the naked eye shows to be a heterogeneous tangle of opaque white curd fibers enmeshing clear solution.

Neat soap is plastic, in that small specimens do not flow under the influence of gravity, although large masses as in the soap pan have an almost level surface and flow readily through a pipe. At first sight neat soap might appear to be a jelly, but closer examination shows that it possesses very little of the elasticity characteristic of a jelly. For instance, a true soap jelly which is likewise perfectly clear and tends to retain its shape, quivers when shaken, and a small piece if deformed springs back to its original shape, whereas the plastic anisotropic neat soap retains any shape given it. Furthermore, it may be mentioned that the true soap jellies, just like clear gelatin jellies are isotropic or singly refracting when not under strain.

When anhydrous soap is heated it first melts to form liquid crystals, and this anisotropic liquid exists for a further 100° of temperature before it "melts" again to the clear isotropic liquid. Further, it can be admixed with water and even salt in various proportions without losing its homogeneity and we can thus pass without any discontinuity from the molten anhydrous soap to the soap boiler's neat soap and beyond. The whole of this form we therefore call neat soap.

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* Some proteins, commonly considered to be definite chemical compounds, fail to show such constancy of composition. J. A.

(4) *"Middle soap."*—McBain and Langdon[12] recently discovered the existence of another anisotropic form of soap solution existing in a narrow region of concentration intermediate between that of "neat soap" and ordinary isotropic soap solutions; for this reason they called it "middle soap." When pure materials are used "middle soap" is a colorless, transparent plastic liquid, whose appearance and consistency resemble medicinal vaseline. Under certain circumstances when examined in polarized light it exhibits the structure of a typical conic anisotropic liquid.[13] It should be emphasized that "middle soap" is immiscible both with "neat soap" and with isotropic soap solution.

(5) *Isotropic Solutions of Soap.*—There is a wide range of concentration both with and without salt, over which soap solutions are isotropic; that is, dark between crossed nicols. Such solutions are of very diverse character, although there is a gradual and continuous passage from one to the other, the properties of each solution being fixed by its concentration and temperature, except in the one instance of gelatinization. Much space would be required for an adequate description of the properties of these soap solutions.[14] All the solutions are hydrolyzed, but since the hydrolysis-alkalinity does not exceed 0.001 N and is for most solutions much less, hydrolysis is wholly inappreciable for ordinary concentrated solutions. It may be mentioned that the product of hydrolysis is never free fatty acid, but is an acid soap of intermediate composition;[15] very dilute soap solutions contain, apart from acid soap, no colloidal constituents, and the soap ionizes like sodium acetate. With rising concentration, however, both undissociated electrolyte and fatty ions each polymerize to colloidal aggregates, neutral colloid, and the ionic micelle respectively. The constitution of "middle soap" is similar; the soap being present as colloidal electrolyte. This is highly dissociated into ordinary sodium or potassium ions and the excellently conducting aggregates of fatty ions that constitute the ionic micelle. The hydration of the colloidal soap has been measured in several solutions[16] and found to be about 10 molecules of water per equivalent of soap. This is a much greater degree of hydration than the soaps exhibit in anisotropic solution (see later). In parallel with this is the hydration of the curd fibers separating from isotropic solution which is about double that of fibers crystallized from anisotropic solution.[17]

Addition of salt gradually drives back the dissociation of the colloidal electrolyte, until it is mainly neutral colloid. Addition of a very small amount of salt slightly diminishes the viscosity of a soap solution,[18] but further addition of salt increases the viscosity so enormously that several investigators[19] gave up the attempt to follow it further and so missed finding that it really rises only to a sharp maximum * and thereafter falls off again to a fraction of its value before the limits of homogeneous solution have been reached. This effect has been studied by Miss King and several others in the Bristol laboratories.[20] (See Fig. 1.) Numerous qualitative observations have been made by M. H. Fischer.[21]

True jellies[22] are formed by the highest soaps even in the absence of salt but they do not appear to constitute a separate phase, and the passage to the gelatinous condition appears to be quite continuous. It is noteworthy that none of the properties of soap solution are altered by gelatinization, with the striking exception of mechanical rigidity and elasticity. Possibly there is a slightly enhanced opalescence but all the significant properties such as electrical conductivity and lowering of vapor pressure which depend upon the internal equilibria of the solution, remain unaffected. The conclusion seems inevitable that the actual colloidal particles are the same in solution and in true jelly but that in the jelly the particles of neutral colloid are linked together, probably to form innumerable ultramicroscopic filaments. A similar conception has been developed by Bogue [23] for gelatin jellies. By suitable manipulation two portions of the same soap solution may be brought at the same concentration and temperature into the forms of sol and jelly respectively. The jelly appears to be the most stable form within a narrow range of temperature and it is most commonly met with in solutions containing salt. Excessive salt liquefies the jelly, the effect being analogous to that on viscosity in non-gelatinizing solutions.

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* This seems to be an instance of the zone of maximum colloidality (see p. 21.) J. A.

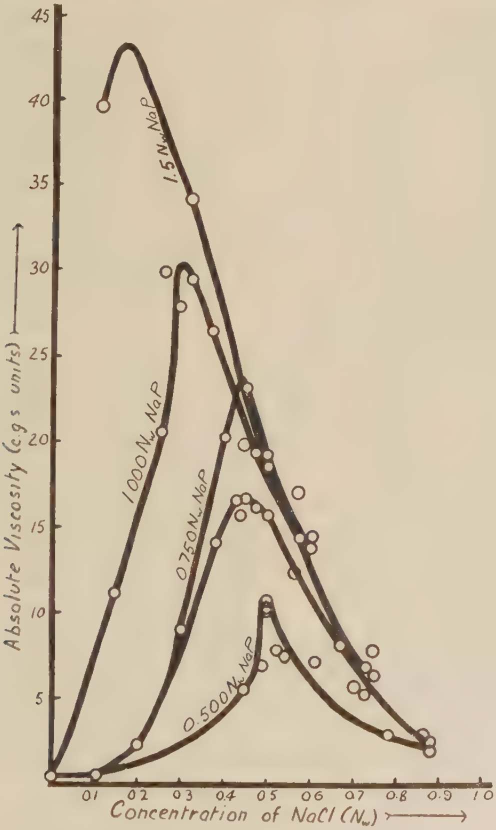

FIG. 1.—The effect of salt upon the viscosity of solutions of sodium palmitate at 81° C.

Having now given a brief account of the appearance and characteristics of all the various phases and forms in which soap and its solutions can exist, we are now in a position to discuss the equilibrium diagram of the two-component system water and soap in the absence of salt. Here again most of the information has to be drawn from observations made in the writer's laboratory.

THE TWO-COMPONENT SYSTEMS: SOAP AND WATER

Figure 2 is the phase rule diagram for potassium oleate and water and is due to W. J. Elford.[24] It shows the limits of existence and the composition of the various forms of soap solution which can exist over the whole range of concentrations and temperatures up to 350° C.

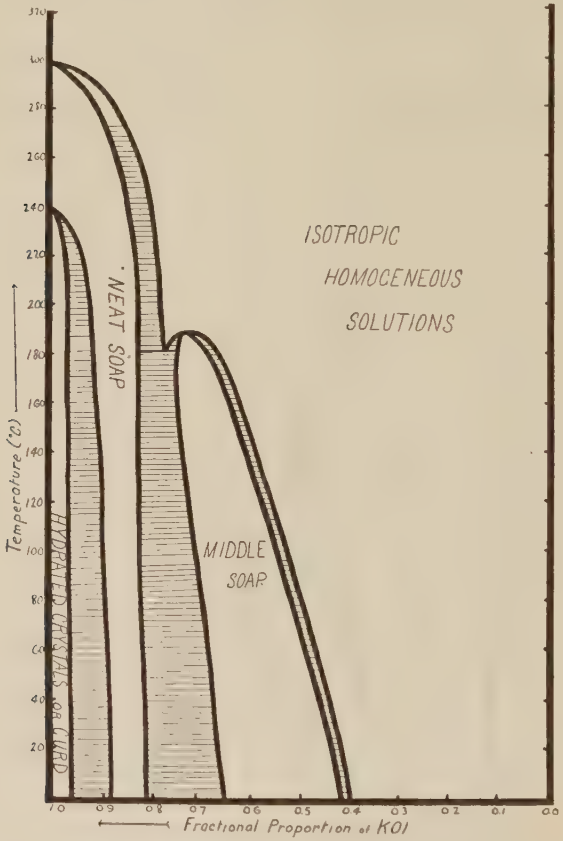

FIG. 2.—Equilibrium diagram for the two-component system, water-potassium oleate, showing the stable homogeneous phases that occur at various temperatures. The boundary of the isotropic solution only is accurately known.

Figure 3 is the diagram for sodium palmitate developed chiefly by Langdon and Pitter.[25] It likewise ranges from anhydrous sodium palmitate to water.

The chief difference between the two diagrams is due to the comparative insolubility of sodium palmitate, which crystallizes out almost quantitatively at room temperature as hydrated curd fibers enmeshing water which contains but a trace of alkali and of soap.

The two diagrams illustrate the great similarity existing between all soaps. This is borne out by the data as far as they are available of W. J. Elford and Miss E. M. Grant for potassium laurate, D. P. Davies for sodium ricinoleate, H. M. Kamil and Miss Grant for sodium abietate, and of W. T. Smith for cetyl sulphonic acid, a hydrogen soap.

The first feature is the very wide range of isotropic solutions which rapidly extends as the temperature is raised, until above about 300° C. water and liquefied anhydrous soap are miscible in all proportions. Even at temperatures as low as the boiling point, the soaps dissolve to form isotropic solutions up to solutions containing about one equivalent of soap in one kilogram of water. "Middle soap" occurs in a region of concentration closely adjoining the isotropic solutions and above a comparatively moderate temperature such as 160° or 190° middle soap can no longer exist but is transformed into isotropic solution. At this temperature it is remarkable to see that middle soap is bounded on the side of both higher and lower concentrations by isotropic solution. No explanation of this is as yet suggested, although it accords with the phase rule. The range of concentration in

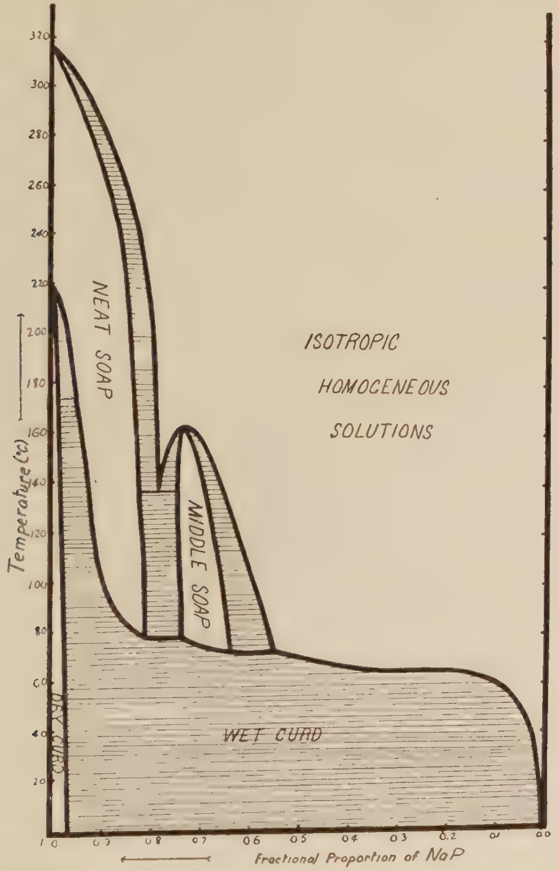

FIG. 3.—Equilibrium diagram for the two-component system, water-sodium palmitate, showing the stable homogeneous phases that occur at various temperatures. The boundary of the isotropic solution only is accurately known.

which middle soap exists is moderately wide, tending towards higher concentrations at higher temperatures.

This is likewise the behavior of neat soap, which at temperatures above the melting point of the solid extends continuously into anhydrous anisotropic soap. The boundaries of the field of middle soap, neat soap and of curd fibers are dotted because their exact position has not been established throughout, but is deduced only from isolated observations.

In Figures 2 and 3 the unshaded areas are homogeneous phases, the shaded areas represent heterogeneous systems of two phases, the tie lines being necessarily horizontal since the two phases in equilibrium are at the same temperature. Figure 3 well illustrates the enormous temperature coefficient of the solubility of soap. This corresponds with the large heat of solution which is in striking contrast to the heat of true gelatinization of a soap solution, which is so small that it has hitherto escaped measurement.

THE THREE-COMPONENT SYSTEM: SOAP, SALT AND WATER

From a qualitative standpoint the three-component system introduces no features that are not to be found in a simple aqueous soap except that the

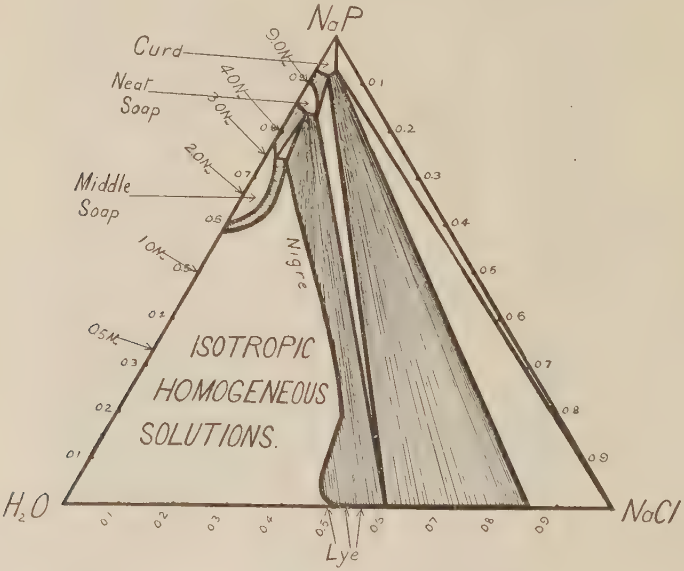

FIG. 4.—Phase rule diagram at 90°, sodium palmitate-salt-water, concentrations being expressed in fractions of mols of sodium palmitate and sodium chloride, but in fractions of one kilogram for water. The shaded areas represent the approximate direction of the tie lines in the two-phase systems.

amount of salt added affects the limits of concentration for the existence of the separate phases. The salt favors the formation of isotropic solutions at the expense of middle soap, and such solutions can be prepared containing large amounts of salt. In fact, this isotropic region extends up to solutions which are saturated with electrolyte, although in such "lyes" there is but very little soap.

The boundary of the field of isotropic solutions in the presence of large excess of salt, is of the utmost interest and importance, since from this derive most of the phenomena of the soap boiling processes. Figures 4 and 5 are the equilibrium diagrams for sodium palmitate, sodium chloride and water at 90° and 100° C, the compositions being expressed in fractional proportions and technical units respectively. In Figure 4 a triangular diagram is used in which the total composition of the system at any point is taken as the sum of the fractions of one gram molecular weight of sodium palmitate and of sodium chloride and of one kilogram of water respectively, the whole adding up to unity for each point. Hence, the three corners represent pure water, anhydrous salt and anhydrous soap respectively, and the sides of the triangle represent the respective two component systems; and a point in the center would represent one mol each of salt and soap with one kilo of water, that is a system weight normal with respect to salt and soap.

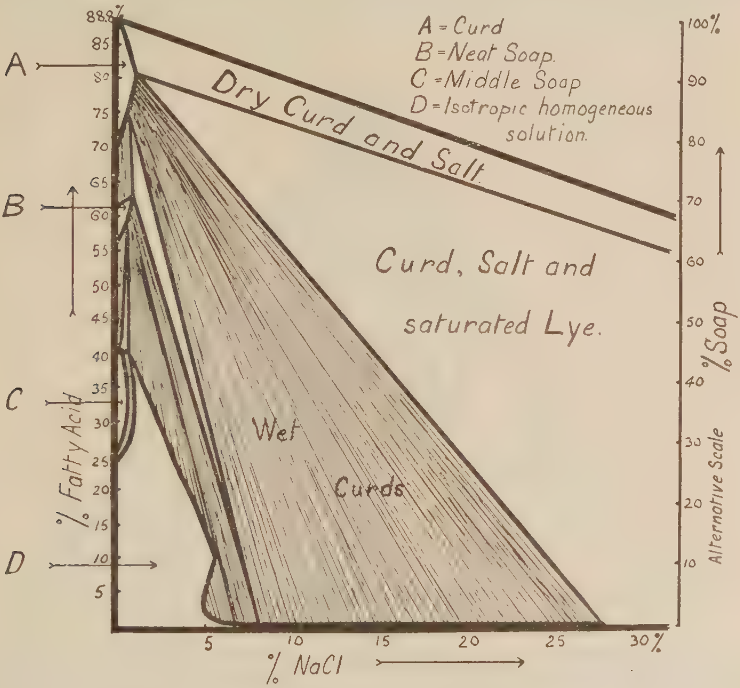

FIG. 5.—Phase rule diagram at 100°, sodium palmitate-salt-water; concentrations being expressed in grams of fatty anhydride and grams of salt per 100 grams of total system. The areas correspond to those in Fig. 4.

Figure 5 in technical units expresses salt in per cent by weight in 100 parts of total system and in per cent by weight of anhydrous fatty acid (so that pure anhydrous sodium palmitate is, for example, 88.85 per cent fatty anhydride). In both diagrams the tie lines between two phases in equilibrium are straight lines and the amounts of those two phases are in exact inverse proportion to the distance of the point representing the total composition of the system from the respective ends of the line.

In addition to the field of isotropic solutions in Figures 4 and 5 for sodium palmitate, there are three other fields representing single phases of varying composition; namely, curd fibers (at the top of the diagram), anisotropic "neat soap," and anisotropic "middle soap." There is but one phase of constant composition; namely, crystalline sodium chloride, which is found at the lower right hand point of the diagram.

There are seven fields in which two phases each of varying composition co-exist; namely, (a) middle soap and isotropic solution, (b) middle soap and neat soap, (c) neat soap and curd fibers, (d) neat soap and isotropic solution (which latter in this region is called "nigre" by soap boilers), (e) neat soap and isotropic solution at the bottom of the diagram (which is always called "lye"), (f) a small region in which the isotropic solution separates into two layers corresponding approximately to nigre and lye, and (g) curd fibers and lye up to its saturation point with salt. Whenever three phases co-exist at barometric pressure each is of fixed composition as shown by the diagram. Solid sodium chloride cannot exist in contact with any phases except saturated lye and curd fibers.

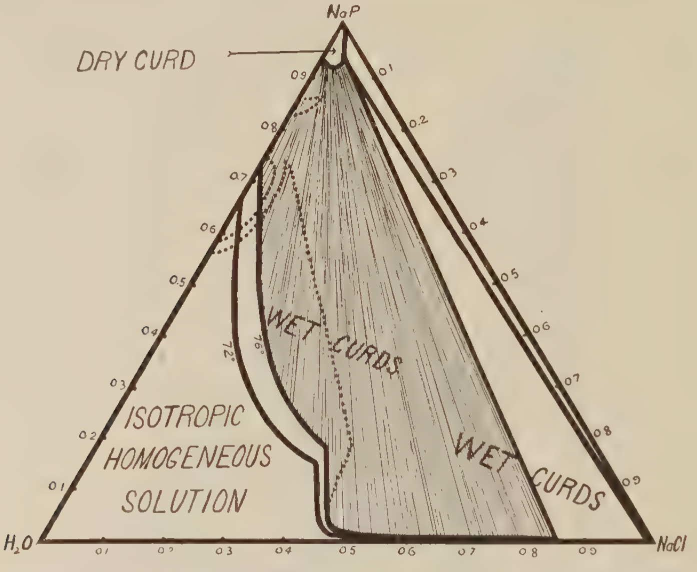

Fig. 6.—Maximum concentrations of solutions which can exist at 76° C. (and at 72°) when not supersaturated with curd fibers. The fields enclosed by the dotted lines within the shaded areas are soap solutions which have been destroyed by the curd fibers crystallizing out at 76°.

The chief of these fields occurring during soap boiling processes (see later) are (d) (during fitting), and (e) (when rather more salt has been added but not enough to salt or grain out), but it is only after the neat soap is cooling in the frames that (c) is met with through the separation of curd fibers, at much lower temperatures.

There is a very narrow triangular field, not shown in the figures, in which three phases, each of invariable composition at any one temperature, may occur. The three phases are neat soap, nigre and lye which may co-exist in various proportions; but the permissible variation in the total proportion of salt present in the system is so small (corresponding to the narrowness of the triangle) that it is of no practical importance.

The form of the fields for neat soap and for curd fibers is only approximately known, but the general position is fixed by an accurate knowledge of one or two points in each.

Figure 6 for solutions of sodium palmitate containing salt represents the effect of cooling to a lower temperature such as 68° C. where the curd fibers of sodium palmitate are so much less soluble, that no soap solutions concentrated enough to form middle soap or neat soap can exist, and even half the isotropic field has been destroyed. At a temperature only about 10° lower, the solubility of sodium palmitate is reduced to an extremely narrow field of lye—along the bottom of the diagram, with curd fibers at the top, all in between being wet curds with enmeshed lye. At room temperature sodium palmitate is practically insoluble and the only systems met with are wet and dry curds. The diagram shows two (approximate) solubility curves for 72° C. and 76° C. respectively and there is also dotted in the boundary lines of the liquid phases at 80° C. at which temperature the solubility of sodium palmitate is so much greater that neat soap is the only form of liquid concentrated enough to be capable of crystallizing.

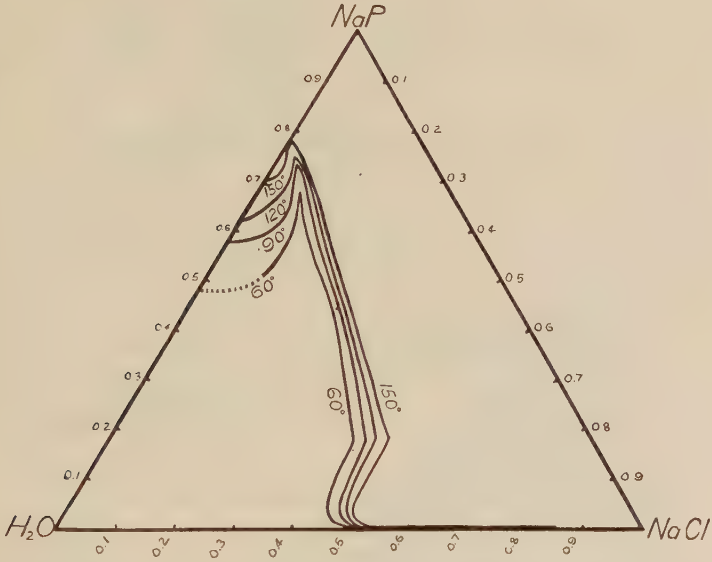

FIG. 7.—Solubility curves of salt and sodium palmitate at 60°, 90°, 120° and 150° showing the extreme limits of the field of homogeneous isotropic solutions capable of existing at those temperatures.

Figure 7 presents the data for the accurate mapping of the limits of the fields of isotropic solutions of sodium palmitate and salt at temperatures ranging from 60° C. to 150° C. The solutions at 60° C. are of course undercooled with respect to separation of curd fibers.

Figures 8, 9, 10 and 11 present W. J. Elford's data for the system potassium oleate, potassium chloride and water. Here the isotherms bound-

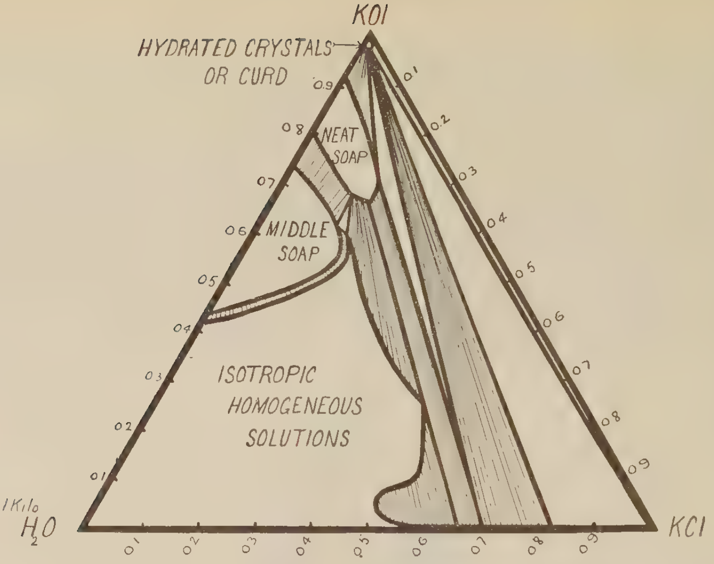

FIG. 8.—Phase rule diagram at 20° C., potassium oleate-potassium, chloride-water; concentrations being expressed in fractions of mols of potassium oleate and potassium chloride, but in fractions of one kilogram for water. The shaded areas represent the approximate direction of the tie lines in the two-layer systems.

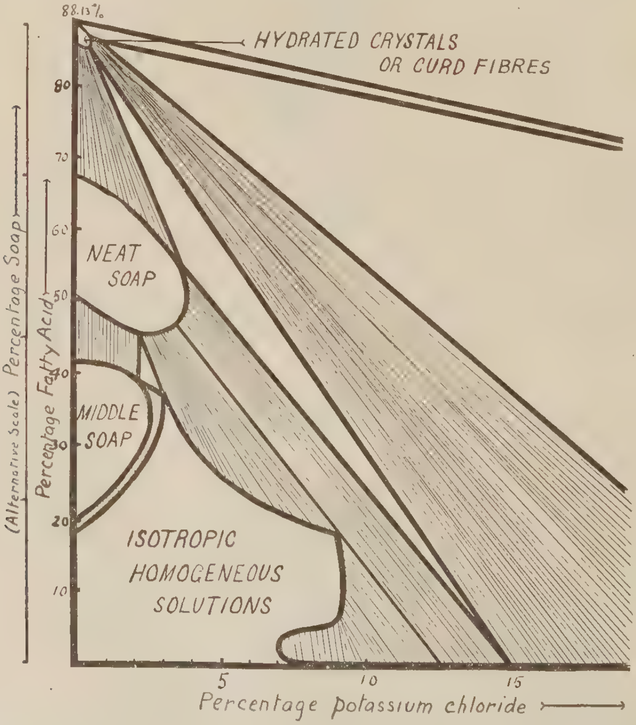
88.13%
HYDRATED CRYSTALS OR CURD FIBRES
80
70
60
NEAT SOAP
50
40
MIDDLE SOAP
30
20
ISOTROPIC HOMOGENEOUS SOLUTIONS
10
(Alternative Scale) Percentage Soap
Percentage Fatty Acid
5
10
15
Percentage potassium chloride

FIG. 9.—Phase rule diagram at 20° C., potassium oleate-potassium chloride-water; concentrations being expressed in grams of fatty anhydride and grams of potassium chloride per 100 grams of total system. The areas correspond to those in Fig. 8.

ing the isotropic field have been fixed over a range of temperature from room temperature up to 210° C. (under many atmospheres vapor pressure of course). The diagrams are of the same type and general form as those for sodium palmitate, the chief difference being that the solutions do not solidify even at room temperature.

EARLIER WORK

It is unnecessary for the present purpose to devote much space to the history of this subject, because the information available is mostly of a fragmentary and contradictory nature and very obscurely described, the meaning being often concealed by loose employment of colloidal terms. There are a few papers however of such outstanding value that they require mention. Nevertheless it should be borne in mind that there has been no recognized theory of this subject.

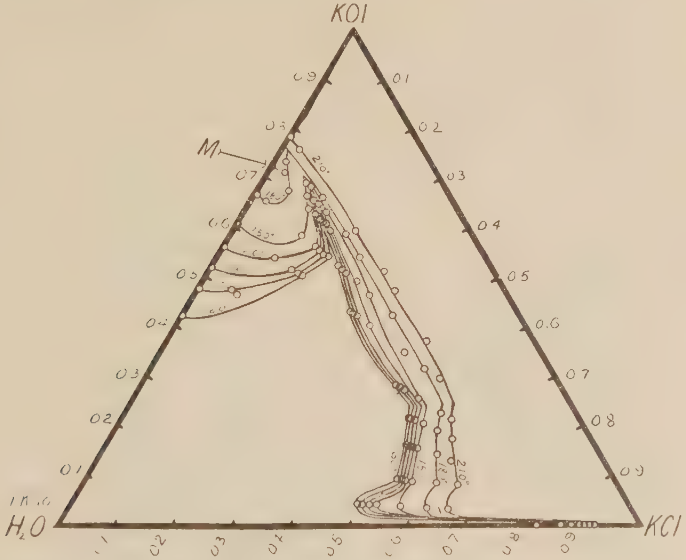

FIG. 10.—Solubility curves of potassium chloride and potassium oleate at 20°, 60°, 90°, 120°, 150°, 180° and 210° C. showing the extreme limits of the field of homogeneous isotropic solutions capable of existing at these temperatures. The point *M* is the only concentration of middle soap which exists up to 183° C., above which temperature it is isotropic.

The present chapter is an attempt to supply a general framework into which all the various scientific and technical data may fit, and which may serve as a basis for the systematic development of the subject.

The scientific investigation of the soap boiling processes may be said to have begun with Merklen's[6] important monograph published in 1907 and 1908, in which for the first time an attempt was made to apply the phase rule. He prepared soaps on a semi-technical scale from each of seventeen of the commonest fats and oils, analyzing the products at each stage of manufacture, and recording their physical appearance and characteristics. This is still the chief source of quantitative information with regard to the composition of soap.

Merklen showed that the composition of commercial soaps depends upon the nature of the fatty acids and of the electrolytes employed, the composition of the nigre, the temperature and on various other factors. He recognized two of the two-layer systems here described; namely, "neat soap" with "nigre" and "lye" respectively. It appears, however, that his soap boiling technique was faulty in that he did not secure proper separation. Further, he failed to realize the nature of commercial soap which is formed simply by cooling neat soap, and allowing it to solidify. He regarded it as a sorption compound in which the soap had adsorbed water, electrolytes, etc. (see previous discussion of curd).

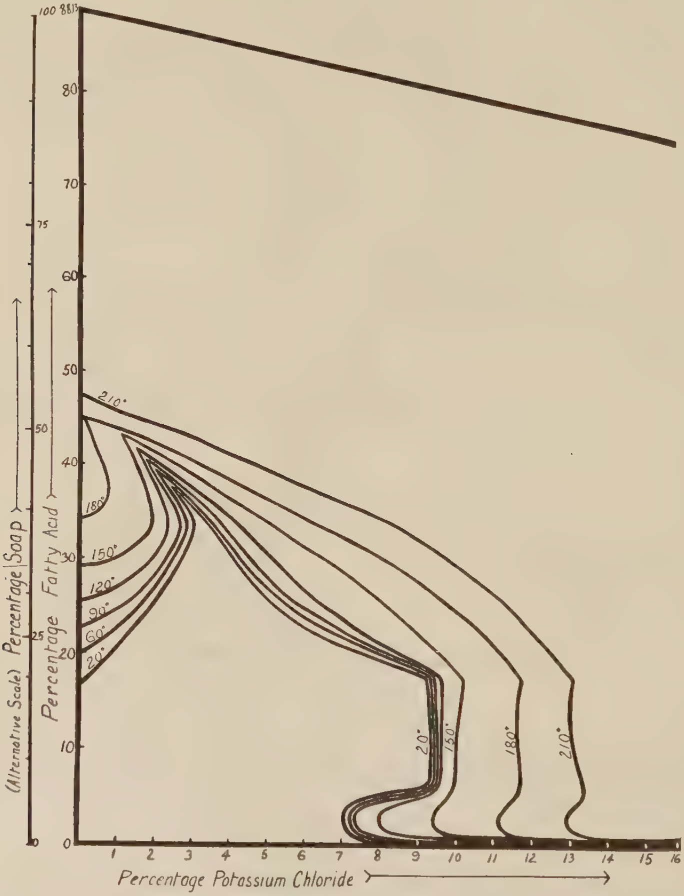

FIG. 11.—Limits of existence in technical units of homogeneous isotropic solutions containing potassium chloride and potassium oleate at 20°, 60°, 90°, 120°, 180° and 210° C. showing the two regions in which solutions of pure soap form isotropic solutions at 210° C.

In 1911 Richert[26] published a very valuable dissertation, embodying the results of laboratory experiments carried out under the direction of Ubbelohde. He worked with dilute solutions and discovered the two-layer system nigre-lye. The investigations comprised the salting out of sodium and potassium salts of pure typical fatty acids by the corresponding hydroxide, carbonate and chloride. A large number of observations are recorded with regard to the formation of the two liquid layers, and the subsequent salting out of curd, processes which, however, were not distinguished by Richert.

F. Bätz (Dissert. Karlsruhe 1918) and M. Thörl (Dissert. Karlsruhe 1918) used soaps made from tallow and from coconut oil, studying neat soap together with lye or nigre or both. They did not take into account the requirements of the phase rule. They considered that the three layers simultaneously present were not of fixed composition, but we can attribute this to a form of experiment in which equilibrium was not perfectly attained. Their results, like those of other published data on analysis of commercial products, agree essentially with the triangular diagram explained in this paper; but, not knowing of the existence of "middle soap" they regarded "neat soap" and "nigre" as continuous with each other instead of being wholly separate phases.

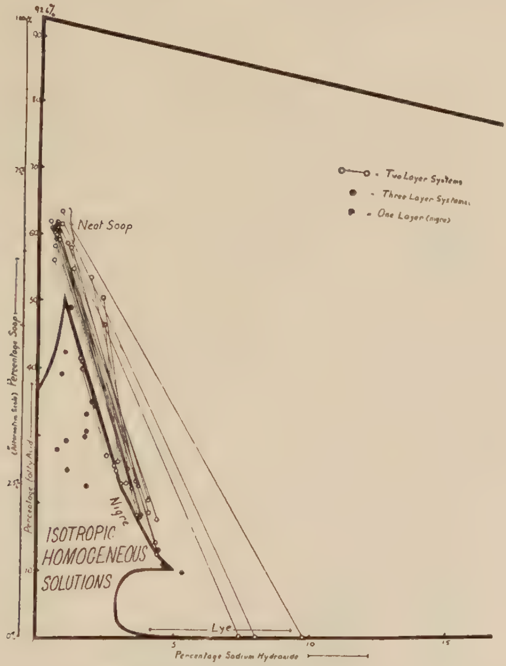

FIG. 12.—A reinterpretation of M. Thörl's laboratory experiments with sodium hydroxide on the salting out of soap prepared from tallow at 100° C. showing how they accord with phase rule diagrams for the pure soaps.*

* The boundary line of the isotropic solutions is inserted in identical position in diagrams 12, 13 and 14, and is deduced from all the available data, including results by Perkowski as quoted by Richert. Results of Thörl, Bätz, Richert and Perkowski are not true per cent but grams per 100 cc. solution measured at 100° C. The data of Penny and Elford are grams per 100 grams of total system.

COMMERCIAL SOAP AND THE PHASE RULE DIAGRAM

We are now in a position to test how well the information obtained from a soap made from a commercial oil or fat agrees with the type of phase rule diagram described in this chapter. For this purpose we shall take the data for tallow and cocoanut oil. This has the additional advantage of enabling us to reproduce in revised form the data of Thörl and Bätz which are otherwise practically inaccessible and which had not been interpreted from the standpoint of the Phase Rule.

Figures 12, 13 and 15 present their experimental data. Each point on the diagram represents their analysis of a homogeneous liquid layer; when two liquid layers co-existed the points are shown in the diagram connected by a fine line. The region in which homogeneous isotropic solutions exist, is indicated by the heavy line which we have drawn in to fit the points given on the diagram; this field includes all the systems which were found to consist of one homogeneous liquid.

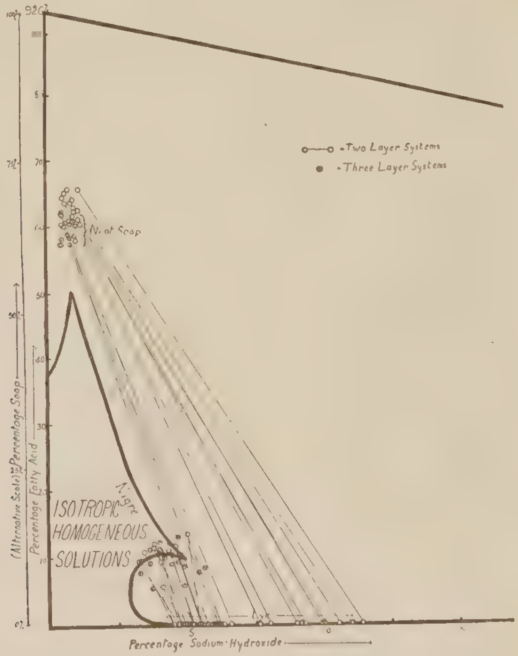

Fig. 13.—A reinterpretation of F. Bätz's laboratory experiments with sodium hydroxide on the salting out of soap prepared from tallow at 100° C. showing how they accord with phase rule diagrams for the pure soaps.*

* See footnote to Fig. 12.

Comparison of Figures 12, 13 and 15 with the previous figures for the sodium palmitate and potassium oleate shows clearly that they all belong to the same type. The general shape of the isotropic field is the same in all cases. The analytical data cluster in definite regions. First along the bottom of the diagram representing the lyes containing much electrolyte and but one or two tenths of a per cent of soap. Then along the boundary of the isotropic field showing the salient at about ten per cent of soap, and finally a thick cluster at the composition of neat soap. No systems of composition such as to involve middle soap were investigated. W. J. Elford in boiling a tallow soap with Mr. Penny of Messrs. Chris. Thomas & Bros., Bristol, obtained the following analytical data. The settled or neat soap contained 61.78 per cent fatty acids, 0.48 per cent sodium chloride, 7.32 per cent total soda (Na_2O) and 0.036 per cent of free soda. This shows that the composition of neat soap found by Thörl and Bätz was correct, and that they had obtained fairly good separation although working on a laboratory scale.

The culmination of the arguments here being developed is to be found in Figures 14 and 16 which contain the data of Merklen on a semi-technical scale, and the more careful experiments of W. J. Elford with Mr. C. Penny of Messrs. Chris. Thomas & Bros. in boiling five-ton lots of pure tallow and pure coconut oil. The heavy line drawn in Figures 12, 13 and 15 respectively, to show the boundaries of the isotropic solutions, agree remarkably with the results of the full scale operations. Indeed, this goes so far as to form a standard by which to judge the full scale results.

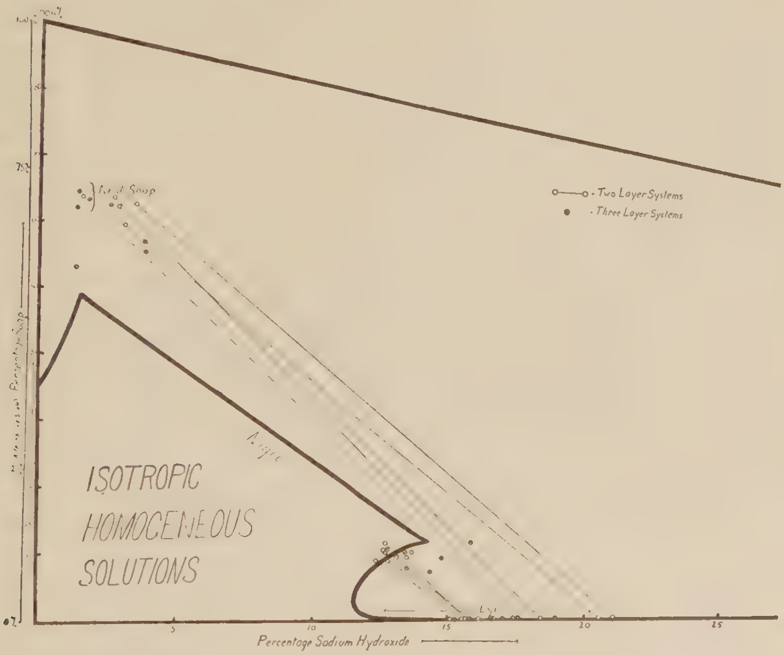

FIG. 15.—A reinterpretation of M. Thörl's laboratory experiments with sodium hydroxide on the salting out of soap prepared from coconut oil at 100° C. showing how they accord with phase rule diagrams for the pure soaps.*

* The boundary line of the isotropic solutions is sketched in an identical position in diagrams 15 and 16 and takes account of results of Perkowski quoted by Richert. Results of Thörl, Bätz, Richert and Perkowski are not true per cent but grams per 100 cc. of solution measured at 100° C. The data of Mr. Penny and Elford are grams per 100 grams of total system.

Similar diagrams have been partly prepared for fifteen other single oils and fats and they are all true to type.

Discussion of these diagrams will be resumed when we have given a brief account of the soap boiling processes which is quoted from McBain and Walls.[27]

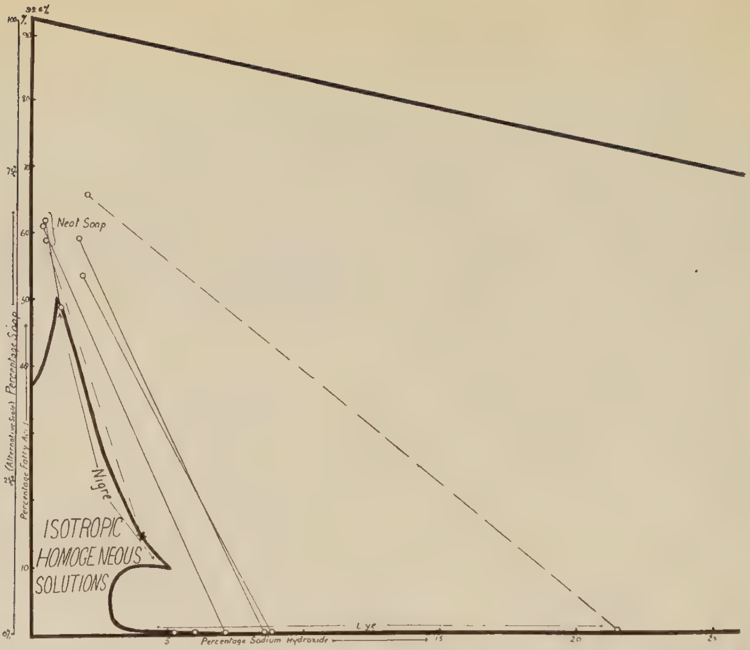

FIG. 14.—Analyses of lye, nigre and soap obtained by Mr. Penny and W. J. Elford in boiling tallow on full commercial scale. The two dotted lines are experiments by Merklen on a small scale.* The concentrations of electrolytes are all reduced to the corresponding value of sodium hydroxide by multiplying with Richert's ratios which however are not more accurate than one-tenth.

* See footnote to Fig. 12.

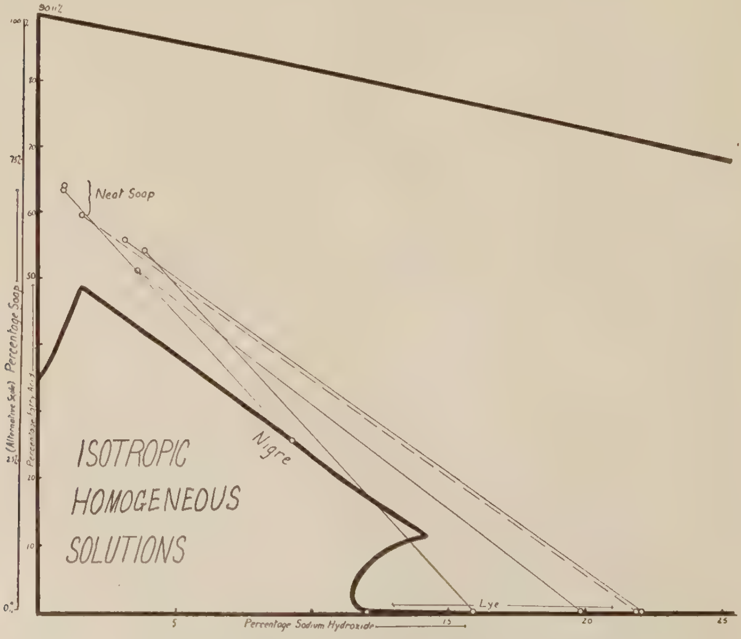

FIG. 16.—Analyses of lye, nigre and soap obtained by Mr. Penny and W. J. Elford in boiling coconut oil on full commercial scale. The dotted lines are experiments by Merklen on a small scale.*

* See footnote to Fig. 15.

Soap Boiling Practice

The methods at present employed in the commercial manufacture of soap are identical in essentials with the original process, discovered, no doubt, by accident, in the Middle Ages. The original cold process has given way to the boiling process; steam has replaced fire heat; new raw materials have been brought into use; color and purity have been improved; but the process still remains the simple saponification of glycerides, or neutralization of fatty acids, by alkali.

In a standard process of soap manufacture the actual saponification takes place in five stages or "changes."

First change.—"Killing" (pasting, saponification, empâtage).

> (*a*) The fat charge * is run into the pan or kettle. Open steam is turned on and weak caustic soda (20° Tw. = 1.1 sp. gr. 8.78 per cent. NaOH 2.2N) is added until an emulsion is formed.

With some oils, *e.g.,* cotton seed oil, the emulsion is difficult to produce and the initial stage is slow. Once the emulsion is formed the process usually proceeds smoothly, alkali being added as fast as it is taken up by the fat.

> (*b*) Caustic soda of 40° Tw.† (= 1.2 sp. gr. 17.81 per cent. NaOH 4.45N) is now added. The object of adding the stronger alkali is to maintain the concentration. If the alkali is added too slowly, "balling" or "bunching" takes place, that is to say, the mixture separates into large separate masses of soap enclosing free fat. To prevent this salt is thrown into the pan during the addition of the alkali. The pan is kept vigorously boiling with open steam during the process. The alkali is in gradually diminishing excess. The soapmaker considers the process complete when a portion of the boiled mass is no longer greasy to touch, and the lyes which separate from the soap are free from turbidity on cooling. At this stage the whole of the caustic alkali should be "spent," *i.e.,* combined with the fatty acids, but the soap should color a 10 per cent solution of phenol-phthalein in neutral alcohol. The soap in the pan forms a pasty mass.

Second change.—Graining (salting out, relargage). To complete the operation salt is added ‡ and this "grains" the soap, that is to say, causes it to separate in closely packed particles up to 5 cm. in diameter, forming a stringy mass at the top of the soap pan.

The spent lyes or watery solution (containing say 0.3 per cent total alkali (Na_2) entirely as carbonate—none should be present as free alkali—some glycerine and much salt) gradually settles out at the bottom of the pan and is run off.

The soap is considered to be completely grained when a sample taken out on a trowel is seen to consist of grains of soap distinctly separated from the clear liquid lyes.

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* A "charge" is usually 25 to 40 tons of mixed oils and fats. It is a common practice to run the charge into the pan in two portions, the second portion being added after the second "change." The only reason for running the charge in two portions is because of the great increase in volume during the saponification process owing to the formation of steam filled bubbles.

† Or higher, up to 57° Tw.

‡ Usually as solid salt recovered from the spent lyes; sometimes as brine of 40° Tw. (1.2 sp. gr. 26 per cent NaCl, approx. 5N).

APPROXIMATE COMPOSITION OF SPENT LYES (STOCK LYE)

	Per Cent
NaOH	0.0–0.15
Na_2CO_3	0.5–0.99
NaCl	8.0–18
Glycerol	4.0–5.5
Sp. gr.	1.09

Third change.—Washing.

(*a*) The soap at this stage contains, say, 0.5 per cent glycerol * of the original 10 per cent glycerol combined in the fat. To wash out the glycerine the pan is boiled and open steam and water is added. The object of adding the water is to "close" the soap, that is, to bring it into homogeneous solution. As compared with the "grained" soap of operation 1 (*b*) the "closed" soap has the smooth and transparent appearance of a stiff jelly. Salt is again added and the soap "grained" when it is allowed to settle, the spent lyes, which contain most of the remaining glycerine and some of the coloring matter from the raw materials, forming the bottom layer as before, which is then pumped off.

(*b*) Repetition of (*a*).

Fourth change.—Strengthening change. (Boiling on strength, clear boiling, coction.) †

The pan is boiled with open steam and the soap "closed" by addition of water. Successive small quantities of alkali (32° Tw. 1.162 sp. gr. 14.35 per cent NaOH, 3.6 N) are gradually added and the soap boiled with closed steam for at least two hours. The total alkali added (reckoned as Na_2O) is about 2 per cent of the weight of the soap. As the alkali becomes sufficiently concentrated, it "grains" out the soap in the same way as the salt in the second change. It is then allowed to settle. The "half-spent" lyes which drop out are strongly alkaline. The soap maker considers the strengthening change complete when a portion of the soap slides freely from a trowel and is distinctly alkaline to the tongue. The object of boiling on strength is to ensure complete saponification. There may be as much as 20 per cent unsaponified fat left at the end of the first change.

APPROXIMATE COMPOSITION OF HALF-SPENT LYES (STRENGTH LYE)

	Per Cent
NaHO	5–6
Na_2CO_3	1–2
Glycerol	3
NaCl	4–6
	13–17

Fifth change.—Fitting (pitching, settling, liquidation).

Water is added to the "grained" soap, which is boiled with open steam, thus bringing it into homogeneous solution, or "closing" it.

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* A soap analyzed at this stage contained 33 per cent total fatty acids, of which 31.01 per cent was combined as soap. Lewkowitsch, *J. S. C. I.*, 26, 591 (1907). In our own analyses we have always found the fatty acids much higher and never below 40 per cent. On pressing to remove water the soap contains 60 per cent fatty acids.

† If the soap formula contains rosin, this non-glycerine-bearing constituent is added prior to the strengthening change, usually in a partly saponified condition and the soap again grained out with salt and caustic soda.

The object of fitting is to get the soap into proper condition for the final slow settling, when the mass separates into soap and nigre as described below.

To arrive at the proper condition for settling, the proportion of the soap and aqueous phases must be carefully manipulated.

Usually a close or fine fit is desired.* The water (steam) is added in slight excess, and the soap then brought back to the required condition by adding a quantity of brine or strong lye.

If soap is in the opposite condition, too pasty or "open," more water is added.

According as the end point is kept on the one side or the other the fit is described as a "close" or "fine" fit, or an "open," "rough" or "coarse" fit.

The method of testing is by taking a portion of the soap from the pan on a trowel. The fitting is reckoned complete when a sample taken on a hot trowel slides completely off it, breaking into two or three broad flakes as it does so. As the soap slides off it discloses a clear aqueous film which immediately evaporates, leaving the surface of the trowel clean and dry.

When the soap is on the open side it leaves the surface of the trowel very freely and with separation into small flakes.

When the soap is on the close side it does not slide off the surface freely, but leaves a smear on the trowel.

An open fit gives a "small" nigre on settling.

A close fit separates more slowly than an open fit and gives a "large" nigre. The nigre is 25 to 40 per cent of the total weight of the soap and nigre in the pan at the end of the process.

The soap is finally boiled for a short time with close steam so as to cause the mass to occupy as much space as possible, and it is then allowed to rest, without undue fall of temperature (say 140°/150° F.) for a considerable period, sometimes several days. The soap at this final stage presents a stiff surface of transparent appearance, breaking here and there into wrinkles.

In the final stage there are four layers: (1) at the top a "fob" or foam, absent if the operations have been carefully carried out, (2) good settled soap, (3) nigre, and (4) at the bottom of the pan, usually, a small amount of spent lyes. The settled soap is drawn off ("cleansed") to pass through subsequent processes; the nigre is usually worked up into lower grades of soap.

The pure settled soap passes from the soap pan to a crutcher where it is agitated by rotating paddles for a short time. It is then run into large frames or steel boxes taking 10 cwt. to 15 cwt. of soap and allowed to cool.

The time table is approximately:

First change (killing)	½ ½	day "
Second change (graining)	½ 1	" "
Third change (washing)	1 1	" "
Fourth change (strengthening)	1	"
Fifth change (fitting)	1	"
(settling)	1½	"
	8	days
Cooling in frame	6	"
	14	days

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* For fabricated or "run" soaps a more open fit is desirable.

An average analysis of a pure settled soap is as follows:

		Per Cent	
68.6 per cent anhydrous soap	Fatty acids as anhydride	61.5	(= 63.6 per cent fatty acids)
	Combined Na_2O	7.1	
31.4 per cent water, etc.	Glycerol	1.0	
	Free Na_2O	traces	
	NaCl	0.5	
	Water	29.9	
		100	

The manipulation of the soap pan requires considerable skill. The changes can easily be bungled, and the boiling emulsion or paste needs careful control to keep it in hand.

The main object of the fitting operation is to separate the soap free from dirt and coloring matter. This is achieved at the expense of soap retained in the nigre, and the highest skill is called for in the satisfactory and economical carrying out of this operation.

The object of the washing is to remove the glycerine remaining in the soap after the first separation; the ideal soap boiling process would ensure complete recovery of the whole of this valuable by-product; at present only about 75 per cent is recovered.

Complete saponification is essential. A commercial soap containing unsaponified fat is soft and on storage will be found to have sweated; it quickly goes rancid. The complete process of soapmaking is somewhat lengthy; shortening of the process offers a fruitful field for research and invention.

Curd soaps do not pass through the fitting process. Dehydration is effected by boiling down on a close steam coil, thus removing the slight excess of water. No separation into two layers takes place in this process.

Hard soap is made with caustic soda; soft soap with caustic potash. Soft soap is not salted out, and if made from glycerides retains its glycerine in the same way as hard soda soaps made by the cold process, which consists simply in crutching the fat and alkali together in correct proportions; after a week or ten days complete saponification has taken place. This is assisted by the heat of reaction.

A pure soap manufactured in the way above briefly described always shows about 63 per cent fatty acids combined with the equivalent of Na_2O, together with variable traces of glycerine and salt. The nigre, according to the proportion separated, has from 30 to 45 per cent fatty acid contents.

The commercial product, hard soap, may be defined as the sodium salts of certain fatty acids in intimate association with about 30 per cent of water.

If water is added to such soap to reduce the fatty acids, it forms a paste which will not set; by substituting for water silicate of soda, a mass is formed which will set on cooling and which simulates pure soap.

By heating pure soap in a mixing vessel with a steam jacket, some water is driven off and the fatty acids can be raised, say, to 70 per cent, but there is a loss of structure, and if the heating is continued dry flakes of totally different physical character are formed. By driving out as much as possible of the water by heat, a nearly anhydrous soap which consists of true salts of the mixed fatty acids can be obtained, the structure being entirely broken up.*

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* McBain found on heating at 90° C. in the vacuum of a water pump that sodium palmitate still retained one equivalent of water (= 6 per cent).

At a half-way stage we get a hard, amorphous soap which is used in practice as a base for toilet soaps.

The above descriptions apply to pure soaps. Soaps may be fabricated by crutching with sodium silicate of appropriate concentration, whereby the fatty acids can be reduced as low as 20 per cent, the soap eventually losing its characteristic grain and firmness; or by mixing with strong sodium carbonate and silicate solution whereby the fatty acids can be reduced as low as 55 per cent, with loss of structure, but retaining and even increasing the hardness of the soap. Mixtures with china clay, talc and the like are usually regarded as methods of adulteration.

The hard "run" soaps above mentioned are particularly adapted for taking up other admixtures such as medications (carbolic acid, coal tar, etc.) or naphtha, paraffin and mineral oils. Carbolic acid is frequently mixed with pure soaps. The resultant mixed soap has little structure and is softer than the original soap unless it is dried up and thus dehydrated in the process.

Colored mottled soaps, as usually produced, are silicated soaps containing coloring matter. They can be hardened by pickling in strong brine solution. Marbled soaps produced on the continent are made by mixing two hot soap solutions of approximately equal specific gravity at a temperature slightly below that at which the soaps have been settled out.

The Generalized Application of the Phase Rule Diagram

It is evident that the soap boiler operates wholly in heterogeneous systems which we can now recognize on the phase rule diagrams. The total composition of the contents of the soap pan or kettle comes about half way up in the diagram and the greatest fluctuation is that due to varying the amount of alkali and of salt. During separation there is lye and neat soap in addition to the oil and in some works the attempt is made to keep the concentration of alkali as high as possible without exceeding the limit at which curding or graining begins. This is likewise often the case during boiling on strength. During the washing to recover the glycerine the soap is partly salted out as curd fibers, the most insoluble soaps curding first, the others remaining as portions of neat soap surrounding them. It is only after these processes that the strong solution of electrolytes is drawn off and sufficient water is added to bring the contents of the soap pan into the region neat soap-nigre. It remains a matter for careful determination as to whether this is ever carried so far as to reach the middle soap region.

It is only necessary to draw a straight line across any of the diagrams connecting the given point in the region neat soap-nigre, with the right hand corner of the diagram representing pure salt, in order quantitatively to predict the effect of further addition of salt upon the amount and composition of the nigre. It is seen at once that (except where nearly all the soap is already neat soap) such addition diminishes the amount of nigre at the same time as it lessens its content of soap. Altering the amount of water whilst keeping the proportion of salt constant merely varies the respective proportion of neat soap and nigre in a manner which can be read from the diagram.

We now come to a most important set of generalizations which enable us to apply the phase rule diagram to any soap, pure or commercial, in the presence of any electrolyte or mixture of electrolytes. This is exemplified when we now point out that the results of Thörl, Bätz, Richert, Perkowski, Merklen and Elford, which have all been plotted on the same scale diagrams, were obtained from different series of experiments in which the electrolytes were greatly varied in nature and amount and in which we have merely multiplied the analytical data by numerical factors taken from Richert's dissertation.[28] The results are thus given as though all the experiments had been carried out with solutions of pure sodium hydroxide alone.

In the first place it is evident from scattered information, published and unpublished, that there is little or no fractionation when mixtures of soaps separate into liquid layers. Hence, as far as formation of liquid layers is concerned, the most complicated mixture of commercial oils and fats containing a number of electrolytes such as hydroxide, carbonate, chloride, sulphate, etc., exhibits a behavior similar to that of a three-component system such as is described in the present paper. It is only when sufficient salt has been added to cause a separation of some of the least soluble soaps as curd fibers, that fractionation of the soaps sets in, and the behavior is that of a more complicated system.

There are therefore now two things to discuss, first, the relative behavior of various soaps, and second the effect of various electrolytes and mixtures of electrolytes.

The soap diagrams are so similar, that information with regard to a point on one of the main boundaries, enables us to construct the approximate diagram for the particular soap and electrolytes in question. It is for this reason that we are able to turn to account such experiments as those of Richert which dealt with soap solutions so dilute that they never occur in soap boiling. It is possible by studying Richert's data and diagrams and casual remarks, to deduce the approximate minimum concentrations of various electrolytes required to initiate formation of the two liquid layers, nigre-lye. Likewise, although more roughly, one may deduce the concentrations at which curding commenced. It should be pointed out that some of Leimdörfer's [28] statements are in flat contradiction of Richert's results which were at that time unknown to Leimdörfer. In so far as our own work has included systems similar to those of Richert, we have confirmed, at least approximately, his observations, although his interpretations and ideas conflicted with the phase rule.

Table I presents results deducted from Richert's data showing the concentrations of various electrolytes required to produce the two isotropic liquid layer systems, nigre-lye with various pure soaps, in unspecified dilutions of probably about N/8 or N/4. Richert's concentrations are given in grams per 100 c.c. of solution at 100° C. and not in true per cent and they refer only to the lower layer, since the upper layer was not analyzed. The numbers given are not always the minimum concentrations but merely the weakest solutions he used. Most of the values have been deduced from a study of his graphs in the light of his incidental comments.

Table I reveals a great regularity in the amount of salts required to salt out the various pure sodium and potassium soaps. For instance, the amount of potassium salt required to salt out a potassium soap is always twice as great as that of the sodium salt required to salt out the corresponding sodium soap. Richert's observations must be substantially correct although it is impossible to deduce the numerical values accurately and it is rather difficult to compare them exactly with the data of other workers, since Richert gives only the concentration of lye and not the composition of either the total system or of the soap layer.

TABLE I

THE MINIMUM NUMBER OF GRAMS OF VARIOUS SALTS IN 100 C.C. OF LYE AT 100° C. WHEN TWO LIQUID LAYERS (NIGRE: LYE) ARE JUST FORMED FROM POTASSIUM AND SODIUM SOAPS

Electrolyte	KOH	KCl	K_2CO_3	NaOH	NaCl	Na_2CO_3
Erucate C''_{22}	3	—	—	—	—	—
Stearate C_{18}	7	8	13	3	—	6
Oleate C''_{18}	8	—	15	4	5	7
Palmitate C_{16}	10	12	18	4	5	8
Linolate C''''_{18}	10	13	19	—	—	—
Myristate C_{14}	15	20	26	8	8	16
Laurate C_{12}	21	—	34	12	13	—
Ratios	1.50	2.00	2.78	0.87	1.00	1.84

N.B.—A mixture of Na oleate and Na myristate is half way between pure Na oleate and pure Na myristate.

Table II gives unpublished observations by Adams, Staddon and Pitter showing the minimum concentrations of various salts required to salt out 0.25 N_w sodium palmitate at 90° C. It will be seen that the value with sodium chloride accords with Richert's value for sodium palmitate. The fourth and sixth columns give the ratios between the per cent by weight and the equivalent normality for the various salts in columns three and five, taking sodium chloride arbitrarily as unity in each case.

TABLE II

MAXIMUM CONCENTRATION OF VARIOUS SALTS WHICH CAN BE DISSOLVED IN 0.25 N_w SODIUM PALMITATE AT 90° C. BEFORE SALTING OUT INTO TWO ISOTROPIC LIQUID LAYERS RESULTS

Salt	Mol. Wt.	Per Cent by Weight	Ratio	N_w *	Ratio
NaOH †	40.00	—	0.87	—	1.27
NaCl	58.46	4.95	1.000	0.953	1.000
NaAc	82.03	6.42	1.30	0.895	0.94
$NaNO_3$	85.01	7.74	1.56	1.056	1.11
NaBr	102.90	8.05	1.62	0.915	0.96
Na_2CO_3 †	106.00	9.50	1.84	1.00	1.01
NaI	149.90	11.27	2.28	0.906	0.95
Na_2WO_4	294.00	15.1	3.04	0.645	0.68
Na_2SO_4	142.10	9.89	2.00	0.83	0.87
$Na_2C_4H_4O_6$	194.10	+10.46	+2.12	+0.65	0.68

* Mols per 1000 grams water.
† Data for hydroxide and carbonate deduced from Richert's ratios.

A further check upon the regularity of Richert's observations is given by Table III, in which is tabulated the minimum concentrations of lye at 100° C. for the production of curd fibers. It will be noted that the concentrations in this table are all approximately one fifth greater than in the previous Table I. Further, Langdon found that sodium palmitate is curded by a 7 per cent solution of sodium chloride and Stiepel[29] found for sodium laurate, myristate, palmitate and stearate 18, 9, 7 and 5 per cent respectively as compared with Richert's 14, 10, 6 and 5 per cent. Kronacher's unpublished data shown in illustrations of Martin M. Fischer[21a] * agree approximately with those here quoted.

* "Soaps and Proteins," p. 117.

TABLE III

The Minimum Number of Grams of Various Salts in 100 c.c. Lye at 100° C. for Curd Fibers to Appear in Neat Soap Layer

Electrolyte	KOH	KCl	K_2CO_3	NaOH	NaCl	Na_2CO_3
Erucate C_{22}	—	—	—	—	—	—
Stearate C_{18}	(17)	13	20	4	—	7
Oleate C''_{18}	10	—	19.5	4	5	9
Palmitate C_{16}	11	—	22	5	6	12
Linolate C''''_{18}	13	19	24	—	—	—
Myristate C_{14}	18	>23	>38	9	10	17.8
Laurate C_{12}	25	—	>37	13	14	—
Ratios (Table I)	1.50	2.00	2.78	0.87	1.00	1.84

N.B.—Notice also that the values for sodium salts are about half those for corresponding potassium salts in both tables.

Tables I, II and III demonstrate the regularity discovered by Richert that the relative amounts of hydroxide, carbonate and chloride required to form the two layers nigre-lye is a constant independent of the nature of the soap. Hence, the concentrations of any of these or of their mixtures may be expressed in terms of sodium chloride as "effective salt concentration." A mixture of these electrolytes shows that their relative effect is additive, being the algebraic sum of their constituents, so that for example two layers are produced by a mixture containing just one half as much chloride together with half as much carbonate alone. Table IV gives the ratios found by Richert for sodium salts with sodium soaps and for potassium salts with potassium soaps respectively; the chloride being taken arbitrarily as unity in each case. Our values for other salts are to be found in Table II.

TABLE IV

Relative Minimum Amounts of Hydroxide, Chloride, and Carbonate of Sodium and Potassium, Required for Salting Out (in Arbitrary Units)

	Hydroxide	Chloride	Carbonate
Potassium salts by weight	0.76	1.00	1.39
Sodium salts by weight	0.87	1.00	1.84
Potassium salts mols	1.02	1.00	0.70
Sodium salts mols	1.27	1.00	1.01

The data of Bätz for tallow soap and of Thörl for coconut soap confirm the validity of the same ratios for the formation of the two-layer system nigre-lye. Furthermore, Thörl's data for the system neat tallow soap-nigre extends their validity to this region. Richert himself was able to use some of Merklen's comprehensive data to prove the same point and he also quotes unpublished data of Perkowski for tallow soap to the same effect.

There remains a consideration of the extent to which the behavior of a mixture of soaps can be predicted from their pure constituents. In the first place Richert found with mixtures of equal amounts of oleate and myristate, that the concentrations of hydroxide and carbonate required to produce two liquid layers was almost exactly the mean of the two pure soaps. It is more difficult to compare the behavior of commercial oils and fats with that predicted from their separate constituents, because in most cases only the chief constituents are known and that only approximately. However, Richert quotes data by Perkowski for stearin, coconut oil and tallow in which the concentrations required for salting out come fairly between those obtained for the known chief pure constituents. In general, the writer has derived the impression that the amount of any salt or a mixture of salts required to produce a given effect in a commercial mixture is between $1/10$ and $1/5$ more than would have been expected from a knowledge of the more important constituents. This may be partly due to the presence of glycerine which slightly but distinctly increases the concentration of salt required.

Merklen determined experimentally the maximum concentration of salt for the formation of nigre, using soaps made from each of the common oils. He adjusted the concentration of the electrolyte until he judged from the appearance of the grained out soap that it was just beginning to dissolve in the boiling lye. This he designated "limiting lye" (lessive limite, Grenzlauge). The value of a knowledge of this characteristic constant for each oil or fat needs no emphasis, especially since the range of possible concentrations between presence of nigre and graining out of curd is narrow.

The following are Merklen's values for soaps of various oils, which are possibly determined with an accuracy of 10 to 20 per cent, judging by internal evidence. Sesame 6.8, olive 8.1, poppy seed 6.6, poppy seed reheated 7.7, lard 6.0, lard without salt 7.2, tallow 7.0, linseed 7.5, sulphur oil 13.3, saponification olein 8.6, saponification olein with glycerine 9.1, saponification stearine 6.2, cotton seed oil 6.9, earth nut oil 6.7, castor oil 25.1, castor oil and earth nut oil 17.6 per cent.

Some further regularities assist us to grasp the general characters of the various soap systems. One deals with the relation between the concentrations of electrolytes in the lower layer and neat soap and the other gives an indication of the temperatures at which neat soap solidifies.

The upper or "neat soap" layer of most well fitted soaps contains about 30 per cent by weight of water. About half of this is probably combined in some way with the soap in that layer, the other half acts as a solvent. The weight normality of electrolytes and non-electrolytes present in the neat soap when referred to the total water in that layer, is usually about one third of their weight normality in a lower layer whether this is nigre or lye; this is roughly one tenth of the amount in the lower layer when both are expressed in per cent by weight.

Numerous illustrations of this occur in the data of Merklen for special soaps; the following may serve as examples. Two different soaps were prepared from lard by boiling upon two lyes (not nigre) in which by varying the amount of carbonate and hydroxide the concentration of sodium chloride was increased ninefold. The "effective salt concentrations" of these lyes were 10.01 and 7.51 respectively; that of the corresponding soaps, 1.15 and 0.94, and the per cent of water 33.9 and 36.6. It will be seen that the ratios of the effective salt concentrations of the two respective layers when corrected for the difference in amount of water present become almost identical. In four other soaps made from tallow, linseed oil, cotton seed oil, and earth nut oil, the ratios between the per cent of sodium chloride in lye and soap were 11.2, 11.4, 11.4, and 10.4 respectively. Glycerine has a smaller distribution ratio.

Krafft[30] was the first to notice that there is some unexplained connection between the curding temperatures of pure soap solutions and the melting points of the respective pure fatty acids; these are practically identical for solutions of moderate concentrations such as normal or 10 per cent. Merklen found that soap solutions of the concentration of neat soap, solidify at a temperature from 15° to 20° higher than the melting points of the free fatty acids. This is exemplified in Figure 2 where the curding temperature of these two concentrations of soap solutions are seen to be 60° to 66° and 80° C. as compared with the melting point of palmitic acid which is 62° C. The rule however does not apply to mixtures of soaps and their curding temperatures are not necessarily intermediate between those of the constituents.

We have now seen that all soaps, pure, mixed and commercial, whether potassium or sodium, are essentially of the same type, the differences being in degree and not in kind; and that by means of numerical factors we can predict the effect of any electrolyte or mixture of electrolytes. Further, the same relations hold for all parts of the equilibrium diagram. Finally, to a large extent the behavior of a mixture of soaps can be predicted from their pure constituents.

It is evident that the way has now been opened for a solution of some of the outstanding problems of soap boiling, and that a comprehensive framework is being developed into which can be fitted all the facts obtained by scientific research or through long tried technical experience.

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Determination of Size and Mass of Colloidal Particles

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1. Permanent Suspensions

The most comprehensive definition describes a colloidal solution as a suspension in a liquid medium of solid particles (or liquid globules), the linear dimensions of which lie approximately between 10^{-7} cm. and 10^{-5} cm.; the lower limit is fixed by the smallest particle that has been seen by the ultra-microscope, while the upper limit is fixed by the size of particle which will just not settle under the force of gravitation.

A particle in suspension in a liquid is acted upon by gravitation, the buoyant force due to the medium, and also, when motion takes place, by the resistance due to viscosity. The net gravitation force on a spherical particle (radius a) is given by

$$G = \frac{4}{3}\pi a^3 (d_1 - d_2) g \text{ dynes} \tag{1}$$

where d_1 and d_2 are the densities of the particle and the medium respectively. If such a particle is moving in the liquid with a velocity v Stokes' law gives for the force of liquid friction

$$F = 6\pi n a v \tag{2}$$

where n = the viscosity of the liquid medium. As the force G is constant for a given experiment, and F varies as the velocity of the particle, when the sphere falls in the liquid, it attains a constant limiting velocity when $F = G$; from (1) and (2) we find this limiting velocity v_o to be given by

$$v_o = \frac{2}{9}\,\frac{(d_1 - d_2)g}{n}\,.\,a^2 \tag{3}$$

If this formula holds, one should be able to measure a through determining v_o experimentally.

Since v_o varies directly as a^2, it is apparent that as a decreases, there should be a very rapid decrease in v_o. In Table I are given the values of v_o for silver particles falling in water at 20° C. ($n = .01$).

TABLE I

Velocity of Fall of Silver Spheres in Water

Radius	Vel., Cms. per Sec.	Time to Fall 1 Cm.
1 cm.	200,000	0.000005 sec.
0.1	2,000	.0005 “
.01	20	.05 “
.001	0.2	5 “
.0001	0.002	500 “
.00001	.00002	50,000 sec. = ½ day, app.
.000001	.0000002	5,000,000 sec. = 58 days, app.

Even in the entire absence of convection currents in the liquid, the motion possessed by very small particles as indicated in the above table would be entirely masked by the random motion of the particles due to molecular bombardment—the so-called Brownian movement. The theoretical formula expressing the magnitude of such motion has been tested very rigidly by experiment and is now generally accepted. If D cms. represents the displacement parallel to any direction in time t sec. of a spherical particle of radius a, due to collisions with the molecules of the liquid medium

$$D^2 = \frac{R}{N} \cdot \frac{Tt}{3\pi n} \cdot \frac{1}{a} \tag{4}$$

where R and N are the ordinary gas constants (numerically equal respectively to 83×10^6 and 7×10^{23}), T the absolute temperature and n the viscosity of the medium. It is important to notice the relation between D and t; on account of the random, zigzag nature of the motion, the displacement is proportional to the square root of t and not to t simply. In other words, a calculated value of the velocity D/t is not constant but depends upon the value of t itself.

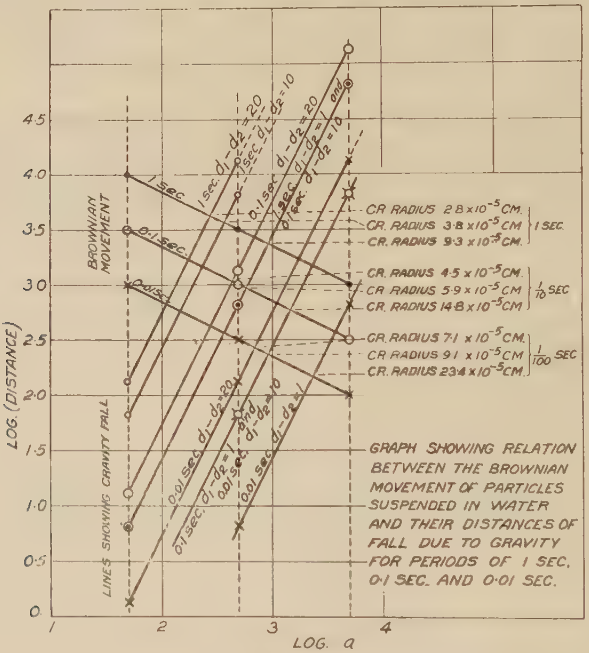

FIG. 1.

The characteristic feature of this Brownian movement is its perfectly random nature: if, then, the magnitude of this motion happens to be equal to or greater than the vertical motion due to gravitation the latter will be completely neutralized and such particles will cease to show any settling even over long periods. Under given conditions of temperature, density of particle, etc., it is possible to calculate the critical radius of a spherical particle such that the Brownian movement for a given period of observation is just equal to the gravitational fall during that period. In Table II are given such results for particles of density 2, 11, and 21 (*i.e.*, $d_1 - d_2 = 1$, 10 and 20 respectively) suspended in water at temperature $T = 300°$ C., calculated for periods of observation 1 sec., 0.1 sec. and 0.01 sec. respectively. For convenience of plotting, the radii and distances are all expressed in terms of $\mu\mu$ which equals 10^{-7} cm.

TABLE II

RELATION BETWEEN GRAVITATIONAL FALL AND BROWNIAN MOVEMENT DISPLACEMENT FOR SUSPENDED PARTICLES.

RADIUS OF PARTICLE $a = a' . \mu\mu$ LOG. a'	BROWNIAN MOVEMENT FROM $D^2 = \frac{R\,Tt}{N\,3\pi n}\frac{1}{a}$ LOG. D			GRAVITATIONAL FALL FROM $v = \frac{2}{9}\frac{(d_1-d_2)g}{n}.a^2$ $vt = x.\mu\mu$ $(\mu\mu = 10^{-7}cm.)$								
				$t = 1$ sec. log. X			$t = 0{\cdot}1$ sec. log. X			$t = 0{\cdot}01$ sec. log. X		
	$t = 1$ sec.	$t = 0{\cdot}1$ sec	$t = 0{\cdot}01$ sec	$d_1-d_2=1$	$d_1-d_2=10$	$d_1-d_2=20$	$d_1-d_2=1$	$d_1-d_2=10$	$d_1-d_2=20$	$d_1-d_2=1$	$d_1-d_2\cdot10$	$d_1-d_2=20$
$(a' = 50)$ 1.7	4	3·5	3	0·83	1·83	2·13	$\bar{1}{\cdot}83$	0·83	1·13	$\bar{2}{\cdot}83$	$\bar{1}{\cdot}83$	·13
$(a' = 500)$ 2·7	3·5	3	2·5	2·83	3·83	4·13	1·83	2·83	3·13	0·83	1·83	2·13
$(a' = 5000)$ 3·7	3	2·5	2	4·83	5·83	6·13	3·83	4·83	5·13	2·83	3·83	4·13

	d_1-d_2	TIME 1 SEC.	TIME 0·1 SEC.	TIME 0·01 SEC.
CRITICAL RADIUS FOR WHICH X = D	1	$9{\cdot}3 \times 10^{-5}$ cm.	$14{\cdot}8 \times 10^{-5}$ cm.	$23{\cdot}4 \times 10^{-5}$ cm.
	10	$3{\cdot}8 \times 10^{-5}$ cm.	$5{\cdot}9 \times 10^{-5}$ cm.	$9{\cdot}1 \times 10^{-5}$ cm.
	20	$2{\cdot}8 \times 10^{-5}$ cm.	$4{\cdot}5 \times 10^{-5}$ cm.	$7{\cdot}1 \times 10^{-5}$ cm.

These results are illustrated in Fig. 1.

Since in the formula for the Brownian movement the density of the particle is not involved, the three parallel lines representing the relation between the Brownian displacement and the radii of the particles for the given periods of time are independent of the different densities. The second set of parallels represents the various values of the vertical descent (x), which depends on the density of the particles as well as the time interval; we have, consequently, 9 x-lines, of which two pairs happen to coincide. If one selects a given period, say 1 sec., the points where this D-line cuts the corresponding x-line will enable one to determine from the graph the size of particle for which the two motions are just equal—our so-called critical radius. Although it remains indefinite as to just what period of time one should select, one must allow long enough to enable the particle to attain its limiting value, and consequently the period chosen cannot be reduced indefinitely; it is probable that the results given by a period of one second are not amiss. With this standard one would judge from the results in Table II that particles sensibly larger than the critical radius would show settling, while those having radii equal to or less than the critical radius would not settle at all. This would give the following critical radii:

$d_1 = 2$ (*e.g.*, Sulphur) 9.3×10^{-5} cm.; $d_1 = 11$ (*e.g.*, Silver), $3{\cdot}8 \times 10^{-5}$; $d_1 = 21$ (*e.g.*, Platinum), $2{\cdot}8 \times 10^{-5}$ cm.

Naturally, the critical radius will increase rapidly as the density of the particle approaches that of water. Some of the solutions of gamboge used by Perrin contained particles visible in the ordinary microscope.

2. METHODS OF DETERMINING THE SIZE OF COLLOIDAL PARTICLES

It is a curious coincidence that the critical radii of substances, which usually are met with in the study of colloidal solutions, are just beyond the limit of visibility with the ordinary high power microscope, and, consequently, their dimensions must be determined in some indirect manner. The various methods applied may be classified as follows:

A. Direct measurement by means of microscope.
B. Indirect measurement by observation of time of settling
    (1) freely under gravity,
    (2) under gravity accompanied by electric field,
    (3) under artificial settling force due to centrifuging.
C. Determination of number of particles per unit volume
    (1) by use of the hæmocytometer,
    (2) after coagulation,
    (3) by gilding particles in solution.
D. Use of various theoretical formulæ involving the radius:
    (1) Brownian movement.
    (2) Optical absorption.

3. METHODS OF DIRECT OBSERVATION

A. It is apparent from Table II that suspensions of some materials of small density will have particles which can be observed and measured directly by means of the micrometer eye-piece. Even for particles just about the limit of visibility of the microscope, the method used by Perrin[2] may sometimes be adopted. He noticed that in a slightly acidulated solution of gamboge, the particles would sometimes coagulate together in a chain. By measuring the length of the chain and counting the number of particles in it, the diameters could be determined; this method takes for granted that the particles are uniform in size. However, as a usual thing, this direct method cannot be applied.

4. METHODS USING VELOCITY OF SETTLING

B_1. If the radii of the particles are above the critical radii defined in section 1, the velocity of settling can be observed and the radius determined by use of equation (3) which may be re-written:

$$a^2 = \frac{9}{2} \cdot \frac{v_o n}{(d_1 - d_2) g} \qquad (5)$$

B_2. The preceding method has very limited application because very few such solutions have particles large enough to settle under gravity. The following method is now being used by the author, and promises to give concordant results.* By the use of the U-tube illustrated in Fig. 2 the mobility of the particles can be determined in an electric field.[3] Part of the U-tube is filled with the dispersion medium and a quantity of the solution *ATB* is introduced under this clear liquid by means of the funnel *F* and tap *T*. Platinized electrodes are kept at a convenient level in the upper clear medium and a constant potential difference maintained over a given period of time. The rate of migration of the two boundaries *A* and *B* can be observed and so the mobility deduced. In practice the potential is kept in one direction for, say, ten minutes and then reversed for twenty; the average of the two displacements at *A* and *B* is taken for the last twenty minutes. With many samples it is noticed that during this operation there occurs a slight settling of the colloidal surfaces *A* and *B*—a settling which is manifestly due to gravity, although the colloid if left to itself would show no settling at all. The explanation is as follows. When the sample is left to itself and shows no settling, it means that the Brownian movement is sufficient to completely mask the gravitational fall, but, when the particles are swept back and forth by the electrical field, if the direction of the gravitational force coincides with that motion, the gravitational force will be acting with or against the electrical force on each particle. Consequently as a particle moves up in one of the tubes in obedience to the electrical force it is being pushed along by a force given by

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* Burton and Reid, *Phil. Mag.*, 1925.

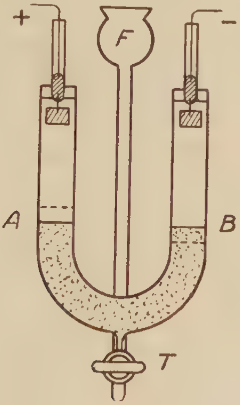

Fig. 2.—Velocity Tube.

$$\text{Electrical Force} - \frac{4}{3}\pi a^3(d_1 - d_2)g;$$

when moving down the tube it is acted upon by a force.

$$\text{Electrical Force} + \frac{4}{3}\pi a^3(d_1 - d_2)g.$$

There will be a net settling, x cms., during the time t such that from equation (3) we shall have:

$$\frac{x}{t} = v_0 = \frac{2}{9} \cdot \frac{(d_1 - d_2)g}{n} \cdot a^2 \tag{6}$$

In order to minimize the disturbance due to diffusion of the products of electrolysis a potential alternating every minute or so is applied and as a result settling takes place, from which the size of particle may be deduced by the above equation. This method will likely prove applicable to particles of radius below 10^{-5} cm.

B_3. The process of settling has been artificially intensified by the application of the centrifuge, suggested first by Svedberg.[4] By using a centrifugal force instead of gravity it is possible to extend the range of the settling method considerably.*

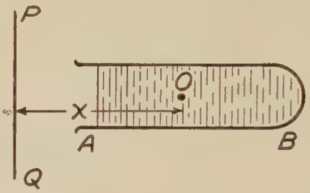

FIG. 3.—Centrifugal Action on Particles.

If O represents the position of a colloidal particle in the revolving tube AB of a centrifuge at time t and at a perpendicular distance x from the vertical axis of rotation PQ, the forces acting upon the particle will be:

$$\frac{4}{3}\pi a^3(d_1 - d_2)\omega^2 x, \text{ the centrifugal force,} \tag{7}$$

and

$$6\pi n a\frac{dx}{dt}, \text{ the frictional force (Stokes),} \tag{8}$$

where ω is the angular velocity of the tube. For uniform motion we have equating (7) and (8).

$$\frac{dx}{dt} = \frac{2}{9}\frac{a^2(d_1 - d_2)\omega^2}{n} . x \tag{9}$$

which is analogous to formula (3).

If, in time t, the particle moves from $x = x_1$ to $x = x_2$ we obtain by integration,

$$\int_{x_1}^{x_2}\frac{dx}{x} = \frac{2}{9}\cdot\frac{a^2(d_1 - d_2)}{n} . \omega^2\int_o^t dt$$

$$i.e., \log\frac{x_2}{x_1} = \frac{2}{9}\frac{a^2(d_1 - d_2)}{n} . \omega^2 t \quad \text{or} \quad a = \sqrt{\frac{9}{2}\cdot\frac{n\log\frac{x_2}{x_1}}{(d_1 - d_2)\omega^2 t}} \tag{10}$$

This method has very far-reaching possibilities in the hands of trained workers; it is necessary to observe the motion of the surface of the colloid while the centrifuge is actually in motion as the re-diffusion of the colloidal particles after the cessation of the revolving motion is very rapid.†

5. METHODS INVOLVING ESTIMATION OF THE NUMBER OF PARTICLES PER UNIT VOLUME BY COUNTING

C_1. By use of Hæmocytometer.[5]

The ordinary hæmocytometer or blood counter enables one to view by means of the microscope an extremely small volume of liquid; it consists of a special microscope slide illustrated in plan and section in Fig. 4. A short truncated cone of glass A is fixed on a glass plate S and surrounded by an outer plate *B*. The upper surface of *B* is so adjusted as to be just 0.1 mm. above that of *A*; the surfaces of *A*, *B* and the cover slip *C* are all optically plane, so that when *C* is placed on *B*, there will exist between the top of *A* and *C* a space exactly 0.1 mm. thick. In addition, the central portion of the surface *A* is divided by diamond point rulings into small squares either 0.1 mm. or 0.05 mm. side. When a drop of colloidal solution is placed on *A* and covered by *C*, the surplus flows down into the annular groove about *A*, and a volume as small as 0.00025 cu. mm. can be discerned through the microscope. By raising or lowering the objective very slightly, it is possible to bring all the particles in a layer 0.1 mm. thick into view, and so for sufficiently dilute solutions the number of particles per cu. mm. can be very approximately determined. The following is a sample of such a determination, typical as regards the method and the magnitude of the quantities involved:

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* See paper by T. Svedberg, this volume. J. A.

† See Svedberg and Rinde, *J. Am. Chem. Soc.*, 46, 2677 (1924).

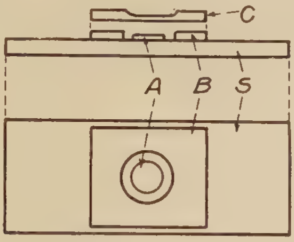

FIG. 4.— The Hæmocytometer.

A silver solution (after Bredig) containing 6.8 mgms. of metal per 100 c.c. was diluted with distilled water to one hundred times its original volume. A drop of the dilute liquid showed on the average the presence of 300 particles per volume 0.1 cu. mm. Therefore in the original solution per cubic centimeter there were 3×10^8 particles weighing 6.8×10^{-5} grm.

If the specific gravity of the silver particles be taken as 10.5, the mean volume of the particles in solution is 2.2×10^{-14} c.c. Assuming that the particles are in the form of small spheres, the mean radius being a,

$$\frac{4}{3}\pi a^3 = 22 \times 10^{-15} \quad \text{or} \quad a = 1.7 \times 10^{-5} \text{ cm.}$$

There are elements of uncertainty in the above method. Under the best circumstances the observations require considerable time, during all of which the Brownian movement will cause particles to move into and out of the field of view; such a difficulty can be overcome only by a large number of observations on each sample. It is not known definitely whether or not merely diluting the sample may cause a change in the size of the particles. The ordinary method of finding the total amount of disperse substance per unit volume is by evaporating the solution and weighing the residue; in this, one assumes that the substance is all confined to the submicrons, while in reality there are probably always present amicrons and some of the material in the state of molecular solution. A more exact determination involves the separation of the disperse phase by means of a collodion filter and analysis of the dry residue and filtrate separately. An additional source of difficulty is in the choice of the density of the material suspended. Experiments such as those of Rose and Cholodny on gold and silver colloids show that there is not much error in taking the density equal to that of the solid for the metal sols; for such solutions as mastic in water, the density reckoned from the dried residue would be only an approximation.

C_2. Counting Particles after Coagulation.

Perrin (*loc. cit.*) noticed that in a slightly acidulated solution of gamboge the granules become fixed to the glass walls of the containing vessel when they approach near enough. After some hours all of the granules in a small volume viewed in a microscope stick to the wall and can then be counted at leisure.

C_3. Gilding Ultramicroscopic Particles of Colloidal Solutions.

Svedberg[6] and his pupils have made extended use of a method first suggested by Zsigmondy. The latter found that if even extremely small particles of gold existed in a medium where gold colloidal solutions were being prepared, the gold readily condensed about these particles as nuclei and under proper conditions did not form new centers of condensation. Zsigmondy suggested that this phenomenon could be applied to artificially enlarge the nuclei present in a volume of liquid and so bring the individual particles up to a size large enough to enable one to estimate their sizes by one of the foregoing methods. If we know the mass of disperse phase of the original sol, we can calculate the size of the original particles. "In that way we have been able to measure the radius of particles down to about $r = 1.0\ \mu\mu$. Of course it is very important that all the gold be deposited on the particles we are measuring—that there shall be no spontaneous formation of particles. According to some investigations by Westgren, the concentration of the $HAuCl_4$ should not be less than 10^{-4} normal and the number of nuclei not less than 5×10^9 per c.c. If we have too few gold nuclei, some of the gold forms new particles so that we get too high a number. If we get the same number n per c.c. of nuclear liquid when we use different amounts of our nuclei liquid together with different amounts of $HAuCl_4$, *i.e.*, if we get a linear relation between the number of particles and the number of cubic centimeters of nuclear liquid that we use, this is a criterion that there is no spontaneous formation of particles.

"Börjeson has shown that it is possible to determine the size of small particles of other metal colloids by using a suitable gold reduction mixture. Not only metals but a few other substances such as sulphides can be determined by depositing gold upon the particles. The method applies not only to the determination of size of particles in hydrosols but also to organosols containing metallic particles."

6. VARIOUS THEORETICAL FORMULÆ

D_1. The Brownian Movement.

Brownian Movement is the name given to the continual zigzag motion possessed by small particles held in suspension in liquids or gases; it has been shown to be due to collisions between the particles and the molecules of the medium. The connection between the extent of the motion, the time of observation, and other factors has been worked out theoretically in various ways by Einstein, Smoluchowski, and Langevin (see Burton[7]). As a result of this work we have the formula already referred to (Equation 4):

$$D^2 = \frac{R}{N} \cdot \frac{Tt}{3\pi n} \cdot \frac{1}{a}$$

where the letters have the significance already defined.*

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* See also paper by R. A. Millikan, this volume, p. 174. J. A.

Measurements of D, a, t, T and n have been made by very many workers on many different kinds of solutions; the truth of the formula is now accepted. As a consequence, it has been suggested that this formula may be used to calculate a for particles for which simultaneous values of D, t, T and n have been observed.

This method must be accepted with reserve on account of the precautions necessary in order to obtain true values of D and t in any given case.

D_2. Optical Absorption and Scattering.

Much work[8] has been done by Garnett, Spence, Mie, Steubing, Gans, Mecklenberg, Svedberg[9] and Rinde, Lampa and others on the absorption of light and scattering of light by colloidal solutions; certain relations have been found to exist between these phenomena and the sizes of the particles but these determinations are not yet definite enough to be used in the actual calculation of the sizes.[10]

7. Conclusions

In the various methods outlined above there are two different kinds of size determinations. Those methods involving a measurement of the rate of settling under any circumstances, or of the displacement due to the Brownian movement, may be used to give the value of the radius of the particles. The assumption that the particles are spherical is inherent in these methods since they all depend ultimately on the truth of Stokes' Law (Equation 2) which is true for spherical particles only. Those methods depending on the counting of the number of particles in a given volume led to an estimation of the mass of the particles: the total mass of the disperse phase can be usually determined independently, and consequently the mass per particle. In order to deduce the size of the particle one must assume that the density of the particle is known; usually the density is assumed to be that of the material in large masses. This assumption has been shown to be true for gamboge by Perrin, and for arsenic sulphide by Burton and Currie.[11]

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Measuring the Electron and Checking the Kinetic Theory by Ultramicroscopic Observations on Minute Droplets

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The term "electron" was suggested in 1891 by Dr. G. Johnstone Stoney as a name for the "natural unit of electricity," *i.e.*, that quantity of electricity which must pass through a solution in order to liberate at one of the electrodes one atom of hydrogen or of any univalent element or radicle. He said:[1]

> "Attention must be given to Faraday's Law of Electrolysis, which is equivalent to the statement that in electrolysis a definite quantity of electricity, the same in all cases, passes for each chemical bond that is ruptured. The author called attention to this form of the law in a communication made to the British Association in 1874 and printed in the *Scientific Proceedings of the Royal Dublin Society* of February, 1881, and in the *Philosophical Magazine* for May, 1881, pp. 385 and 386 of the latter. It is there shown that the amount of this very remarkable quantity of electricity is about the twentiethet $\left(\text{that is } \frac{1}{10^{20}}\right)$ of the usual electromagnetic unit of electricity, *i.e.*, the unit of the Ohm series. This is the same as 3 eleventhets $\left(\frac{3}{10^{11}}\right)$ of the much smaller C.G.S. electrostatic unit of quantity. A charge of this amount is associated in the chemical atom with each bond. There may accordingly be several such charges in one chemical atom, and there appear to be at least two in each atom. These charges, which it will be convenient to call "electrons," cannot be removed from the atom, but they become disguised when atoms chemically unite. If an electron be lodged at the point P of the molecule which undergoes the motion described in the last chapter, the revolution of this charge will cause an electromagnetic undulation in the surrounding ether."

Faraday showed that one coulomb of electricity (*i.e.*, the quantity conveyed in one second by one ampere) would liberate from solutions of univalent elements weights exactly proportional to their respective atomic weights. He therefore asserted that in the process of electrolysis each atom carries the same amount of electricity, and called the charged atomic or atomic group an "ion" (Gr. ion = *goer* or *traveler*).

Though Faraday's experiments gave no notion as to the quantity of electricity, c, represented by one electron, it enabled us to calculate the ratio of the ion charge, E, to the mass, m, of its associated atom in a given solution. Thus for silver

$$\frac{E}{m} = \frac{1}{0.01118} = 89.44$$

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* This paper is based on Prof. Millikan's book, "The Electron" (Univ. of Chicago Press), from which all quotations, not otherwise credited, are taken. J. A.

electromagnetic units; for hydrogen

$$\frac{E}{m} = \frac{1}{0.01118} \times \frac{107.88}{1.008} = 9.573,$$

or approximately 10^4 electromagnetic units.

If m refers to the mass of the imaginary element which is the unit of our atomic weight system, that is to an atom $\frac{1}{16}$ as heavy as the oxygen atom, or $\frac{1}{107{\cdot}88}$ as heavy as the silver atom, we have

$$\frac{E}{m} = \frac{e}{m} = \frac{107.88}{0.01118} = 9{,}650.$$

But with this gas one gram molecule is one gram; and if N represents the Avogadro constant (number of molecules in one gram molecule), we have $N_m = 1$, or $m = \frac{1}{N}$. Whence

$$\begin{aligned} Ne &= 9650 \text{ absolute electromagnetic units} \\ &= 28{,}950 \times 10^{10} \text{ absolute electrostatic units *} \end{aligned}$$

Using the estimates for N then current, Dr. Stoney in 1874 figured $e = 0.3 \times 10^{-10}$ E.S. units.

On Feb. 8th, 1897, Prof. Townsend described to the Cambridge Philosophical Society the first attempt at a direct determination of e.[2] His novel and ingenious method contains all the essential elements of some of the subsequent determinations.

While it had long been known, even to Laplace and to Lavoisier, that the hydrogen gas evolved when a metal dissolves in an acid carries an electrical charge, this "natural method" of obtaining a charge on a gas was practically neglected until the discovery in 1896 that electrical properties can be imparted to gases by X-rays. Enright [3] had indeed observed that H evolved when Fe dissolves in sulphuric acid carries a positive charge; but Lodge [4] urged that this was simply a frictional spray phenomenon.

Townsend first showed, however, that the O and H released on electrolysis are charged, being positive when the electrolyte is sulphuric acid and negative when the electrolyte is caustic potash., Although only one in about a million million molecules were charged, he thus obtained many more ions per cubic centimeter than he could get with X-rays—*e.g.*, as high as 5×10^{-3} E.S. units. These charged particles formed a cloud by condensing atmospheric moisture. On bubbling the cloud through concentrated sulphuric acid or any drying agent, the moisture was removed and with it about 20 to 25 per cent of the original charge on the gas; but in the presence of moisture, the cloud reformed.

To find the charge on each ion, Townsend proceeded as follows:

(1) He assumed that in saturated water vapor every ion condensed moisture about it, *i.e.*, the number of droplets equaled the number of ions.

(2) He determined the total electrical charge carried by the gas per cubic centimeter by means of a quadrant electrometer.

(3) He determined gravimetrically the total weight of the cloud by absorbing it in tared drying tubes.

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* One electromagnetic unit $= 3 \times 10^{10}$ electrostatic units.

(4) He determined the average weight of the droplets by observing their rate of fall under gravity and applying Stokes' formula.

(5) He divided the weight of the cloud by the average weight of the droplets to obtain the number of droplets (which according to (1) is the number of ions), and then divided the total charge by the number of ions to find e, the average charge carried by each ion.

Townsend's first results were

Using positive oxygen $e = 2.8 \times 10^{-10}$ E.S. units
Using negative oxygen $e = 3.1 \times 10^{-10}$ E.S. units

which he later revised to 2.4 and 2.9 respectively.

The weak points in this method were the assumptions that every ion forms a drop, that Stokes' law applies to such tiny drops, that the drops are all alike, fall uniformly and are uninfluenced by evaporation or convection currents.

Sir J. J. Thomson,[5] utilizing C. T. R. Wilson's observation that sudden expansion (and consequent cooling) causes ions to act as fog nuclei, and computing the weight of the cloud by a different method, obtained somewhat variable results, approximating those of Townsend.

H. A. Wilson[6] modified Thompson's method by introducing a negative cloud between two horizontal brass plates 3½ cm. in diameter and from 4 to 10 mm. apart, connecting the plates with the terminals of a 2000 volt battery, and observing the rate of fall of the top of the cloud when the electric pull was added to that of gravity. He thus measured actually the fall of only the least heavily charged droplets, and further assumed the identity in size of drops produced by repeated expansions.

If mg represents the force of gravity acting on the droplets in the top surface of the cloud and $mg + Fe$ the force of gravity plus the electrical force arising from the action of the field F on the charge e, and if v_1 is the velocity of fall under the action of gravity alone, and v_2 the velocity when both gravity and the electrical field are acting, then, if the ratio between the force acting and the velocity produced is the same when the particle is charged as when it is uncharged, we have

$$\frac{mg}{mg + Fe} = \frac{v_1}{v_2} \qquad (1)$$

Combining this with the Stokes' law equation which runs

$$v_1 = \frac{2}{9}\,\frac{ga^2\sigma}{\eta} \qquad (2)$$

in which a is the radius, σ the density, v_1 the velocity of the drop under gravity g, and η is the viscosity of the air, and then eliminating m by means of

$$m = \frac{4}{3}\,\pi a^3\sigma \qquad (3)$$

Wilson obtained after substituting for η and σ the appropriate values (not accurately known, it is true, for saturated air at the temperature existing immediately after the expansion),

$$e = 3.1 \times 10^{-9}\frac{g}{F}\,(v_2 - v_1)v_1^{1/2} \qquad (4)$$

His eleven results vary from 2.0 to 4.4×10^{-10}, the mean being $e = 3.1 \times 10^{-10}$.

The Balanced Drop Method

The variability of these results on repetition led the author to try stronger electrical fields to hold the top surface of the cloud stationary, so that the rate of its evaporation could be accurately observed and allowed for in the computation. Preliminary experiments using radium as an ionizing agent gave as a mean of ten observations $e = 4.06 \times 10^{-10}$ (extreme values 3.66 to 4.37). But these new attempts led to a modification of the cloud method which proved of far-reaching importance. *It made it for the first time possible to make all measurements on individual droplets,* and thus not merely to eliminate ultimately all of the questionable assumptions and experimental uncertainties involved in the cloud method of determining *e*, but, more important still, it made it possible to examine the properties of individual isolated electrons and to determine whether different ions actually carry one and the same charge. That is to say, it now became possible to determine whether electricity in gases and solutions is actually built up out of electrical atoms, each of which has exactly the same value, or whether the electron, which first made its appearance in Faraday's experiments and then in Townsend's and Thomson's experiments on gases, is after all only a *statistical mean* of charges which are themselves greatly divergent. This latter view had been strongly urged up to and even after the appearance of the work now under consideration.

In the spring of 1909 the first determination was made upon the charges carried on individual droplets, and the following excerpts are from a report of the work at the time.[7]

The Balancing of Individual Charged Drops by an Electrostatic Field

My original plan for eliminating the evaporation error was to obtain, if possible, an electric field strong enough exactly to balance the force of gravity upon the cloud and then by means of a sliding contact to vary the strength of this field so as to hold the cloud balanced throughout its entire life. In this way it was thought that the whole evaporation-history of the cloud might be recorded, and that suitable allowances might then be made in the observations on the rate of fall to eliminate entirely the error due to evaporation. It was not found possible to balance the cloud, as had been originally planned, but it was found possible to do something much better: namely, to hold individual charged drops suspended by the field for periods varying from 30 to 60 seconds. I have never actually timed drops which lasted more than 45 seconds, although I have several times observed drops which in my judgment lasted considerably longer than this. The drops which it was found possible to balance by an electrical field always carried multiple charges, and the difficulty experienced in balancing such drops was less than had been anticipated.

The procedure is simply to form a cloud and throw on the field immediately thereafter. The drops which have charges of the same sign as that of the upper plate or too weak charges of the opposite sign rapidly fall, while those which are charged with too many multiples of the sign opposite to that of the upper plate are jerked up against gravity to this plate. The result is that after a lapse of 7 or 8 seconds the field of view has become quite clear save for a relatively small number of drops which have just the right ratio of charge to mass to be held suspended by the electric field. These appear as perfectly distinct bright points. I have on several occasions obtained but one single such "star" in the whole field and held it there for nearly a minute. For the most part, however, the observations recorded below were made with a considerable number of such points in view. Thin, flocculent clouds, the production of which seemed to be facilitated by keeping the water-jackets a degree or two above the temperature of the room, were found to be particularly favorable to observations of this kind.

Furthermore, it was found possible so to vary the mass of a drop by varying the ionization, that drops carrying in some cases two, in some three, in some four, in some five, and in some six, multiples could be held suspended by nearly the same field. The means of gradually varying the field which had been planned were therefore found to be unnecessary. If a given field would not hold any drops suspended it was varied by steps of 100 or 200 volts until drops were held stationary, or nearly stationary. When the P.D. was thrown off it was often possible to see different drops move down under gravity with greatly different speeds, thus showing that these drops had different masses and correspondingly different charges.

The life-history of these drops is as follows. If they are a little too heavy to be held quite stationary by the field they begin to move slowly down under gravity. Since, however, they slowly evaporate, their downward motion presently ceases, and they become stationary for a considerable period of time. Then the field gets the better of gravity and they move slowly upward. Toward the end of their life in the space between the plates, this upward motion becomes quite rapidly accelerated and they are drawn with considerable speed to the upper plate. This, taken in connection with the fact that their whole life between plates only 4 or 5 mm. apart is from 35 to 60 seconds, will make it obvious that during a very considerable fraction of this time their motion must be exceedingly slow. I have often held drops through a period of from 10 to 15 seconds, during which it was impossible to see that they were moving at all. Shortly after an expansion I have seen drops which at first seemed stationary, but which then began to move slowly down in the direction of gravity, then become stationary again, then finally began to move slowly up. This is probably due to the fact that large multiply charged drops are not in equilibrium with smaller singly charged drops near them, and hence, instead of evaporating, actually grow for a time at the expense of their small neighbors. Be this as it may, however, it is by utilizing the experimental fact that there is a considerable period during which the drops are essentially stationary that it becomes possible to make measurements upon the rate of fall in which the error due to evaporation is wholly negligible in comparison with the other errors of the experiment. Furthermore, in making measurements of this kind the observer is just as likely to time a drop which has not quite reached its stationary point as one which has just passed through that point, so that the mean of a considerable number of observations would, even from a theoretical standpoint, be quite free from an error due to evaporation.

The Method of Observation

The observations on the rate of fall were made with a short-focus telescope, which was placed about 2 feet away from the plates. In the eyepiece of this telescope were placed three equally spaced cross-hairs, the distance between those at the extremes corresponding to about one-third of the distance between the plates. A small section of the space between the plates was illuminated by a narrow beam from an arc light, the heat of the arc being absorbed by three water cells in series. The air between the plates was ionized by 200 mg. of radium, of activity 20,000, placed from 3 to 10 cm. away from the plates. A second or so after expansion the radium was removed, or screened off with a lead screen, and the field thrown on by hand by means of a double-throw switch. If drops were not found to be held suspended by the field, the P.D. was changed or the expansion varied until they were so held. The cross-hairs were set near the lower plate, and as soon as a stationary drop was found somewhere above the upper cross-hair, it was watched for a few seconds to make sure that it was not moving, and then the field was thrown off and the plates short-circuited by means of the double-throw switch, so as to make sure that they retained no charge. The drop was then timed by means of an accurate stop watch as it passed across the three cross-hairs, one of the two hands of the watch being stopped at the instant of passage across the middle cross-hair, the other at the instant of passage across the lower one. It will be seen that this method of observation furnishes a double check upon evaporation; for if the drop is stationary at first, it is not evaporating sufficiently to influence the reading of the rate of fall, and if it begins to evaporate appreciably before the reading is completed, the time required to pass through the second space should be greater than that required to pass through the first space. It will be seen from the observations which follow that this was not, in general, the case.

It is an exceedingly interesting and instructive experiment to watch one of these drops start and stop, or even reverse its direction of motion, as the field is thrown off and on. I have often caught a drop which was just too light to remain stationary and moved it back and forth in this way four or five times between the same two cross-hairs, watching it first fall under gravity when the field was thrown off and then rise against gravity when the field was thrown on. The accuracy and certainty with which the instants of passage of the drops across the cross-hairs can be determined are precisely the same as that obtainable in timing the passage of a star across the cross-hairs of a transit instrument.

"In connection with these experiments I chanced to observe a phenomenon which interested me very much at the time and suggested quite new possibilities. While working with these 'balanced drops' I noticed on several occasions on which I had failed to screen off the rays from the radium that now and then one of them would suddenly change its charge and begin to move up or down in the field, evidently because it had captured in the one case a positive, in the other a negative, ion. This opened up the possibility of measuring with certainty, not merely the charges on individual droplets as I had been doing, but the charge carried by a single atmospheric ion. *For by taking two speed measurements on the same drop, one before and one after it had caught an ion, I could obviously eliminate entirely the properties of the drop and of the medium and deal with a quantity which was proportional merely to the charge on the captured ion itself.*

"Accordingly, in the fall of 1909 there was started the series of experiments described in the succeeding section.

"The problem had already been so nearly solved by the work with the water droplets that there seemed no possibility of failure. It was only necessary to get a charged droplet entirely free from evaporation into the space between the plates of a horizontal air condenser and then, by alternately throwing on and off an electrical field, to keep this droplet pacing its beat up and down between the plates until it could catch an atmospheric ion in just the way I had already seen the water droplets do. The change in the speed in the field would then be exactly proportional to the charge on the ion captured."

General Proof of the Atomic Nature of Electricity

The sources of error or uncertainty inherent in the "balanced-droplet method" are:

(1) the lack of stagnancy in the air through which the drop moved
(2) the lack of perfect uniformity in the electrical field used
(3) the gradual evaporation of the drops, limiting their life to about a minute and the observation of their fall to five or six seconds
(4) the assumption that Stokes' formula applies to such tiny drops.

The method devised to overcome these limitations constituted an entirely new way of studying ionization, and one which at once yielded important results in a considerable number of directions.

First, oil was used instead of water, and when sprayed into the ionization chamber by an atomizer gave positively charged drops having a radius of the order of $\frac{1}{1{,}000}$ mm., which showed no appreciable evaporation. They entered the chamber through a pin hole which constituted its only outlet, thus insuring absence of air currents. A 10,000-volt storage battery gave a constant field, and the failure of Stokes' formula, when applied to such tiny drops, was confirmed and allowed for. The record of one drop will show the significance of these experiments. The mean time (17 determinations) required for the drop to fall 0.5222 cm. under the action of gravity was 13.595 seconds, the extremes being 13.4 and 13.8 seconds, *i.e.,* within the limits of error of the stop-watch used in timing. The following figures give the successive times which the droplet required to rise under the influence of the electrical field produced in this case by applying a P.D. of 5,051 volts to the plates: 12.5, 12.4, 21.8, 34.8, 84.5, 85.5, 34.6, 34.8, 16.0, 34.8, 34.6, 21.9.

Since the drop was positive, the increase in time on the third trip up indicates the capture of a negative ion from the air. The fourth trip indicates the capture of another negative ion, and the fifth trip the capture of still another.

On the seventh trip evidently this last acquisition was neutralized by the capture of a positive ion of like charge.

Assuming * that the velocity with which the drop moves is proportional to the force acting on it and when the field is off is independent of the electrical charge which it carries (as had been done by Townsend, Thomson, and Wilson), we get

$$\frac{v_1}{v_2} = \frac{mg}{Fe_n - mg} \quad \text{or} \quad e_n = \frac{mg}{Fv_1}(v_1 + v_2) \tag{5}$$

where $v_1 =$ the velocity under gravity.
$v_2 =$ the velocity under the electric field.
$F =$ the strength of the field.
$m =$ the mass of the particle.
$g =$ the acceleration due to gravity.
$e_n =$ the charge on the drop (not to be confused with the charge on an ion).

The negative sign is used in the denominator because, for convenience, v_2 will be taken as positive when the drop is going up in the direction of F, while v_1 will be taken as positive when it is going down in the direction of g.

If by the capture of an ion the charge on the drop changes from e_n to e_{n1}, then the value of the captured charge e_i is

$$e_i = e_{n1} - e_n = \frac{mg}{Fv_1}(v'_2 - v_2) \tag{6}$$

v'_2 being the velocity after the capture of the ion.

Since for this drop $\frac{mg}{Fv_1}$ is a constant, any charge which it may capture will be proportional to $(v'_2 - v_2)$, that is, to the change in velocity in the field F due to the captured ion.

The successive values of v_2 and of $(v'_2 - v_2)$ for the drop we have been considering are:

TABLE I

v_2	$(v_1' - v_2)$
$\frac{.5222}{12.45} = .04196$	
	$.01806 \div 2 = .00903$
$\frac{.5222}{21.5} = .02390$	
	$.00885 \div 1 = .00885$
$\frac{.5222}{34.7} = .01505$	
	$.00891 \div 1 = .00891$
$\frac{.5222}{85.0} = .006144$	
	$.00891 \div 1 = .00891$
$\frac{.5222}{34.7} = .01505$	
	$.01759 \div 2 = .00880$
$\frac{.5222}{16.0} = .03264$	
	$.01759 \div 2 = .00880$
$\frac{.5222}{34.7} = .01505$	
	$.00891 \div 1 = .00891$
$\frac{.5222}{21.85} = .02390$	

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* This assumption was subjected to very delicate experimental test and confirmed.

"It will be seen from the last column that within the limits of error of a stop-watch measurement, all the charges captured have exactly the same value save in three cases. In all of these three the captured charges were just twice as large as those appearing in the other changes. Relationships of exactly this sort have been found to hold absolutely without exception, no matter in what gas the drops have been suspended or what sort of droplets were used upon which to catch the ions. In many cases a given drop has been held under observation for five or six hours at a time and has been seen to catch not eight or ten ions, as in the above experiment, but hundreds of them. Indeed, I have observed, all told, the capture of many thousands of ions in this way, and in no case have I ever found one the charge of which, when tested as above, did not have either exactly the value of the smallest charge ever captured or else a very small multiple of that value. *Here, then, is direct, unimpeachable proof that the electron is not a 'statistical mean,' but that rather the electrical charges found on ions all have either exactly the same value or else small exact multiples of that value.*

"II. Proof that All Static Charges Both on Conductors and Insulators Are Built Up of Electrons

"The foregoing experiment leads, however, to results of much more fundamental importance than that mentioned in the preceding section. The charge which the droplet had when it first came under observation had been acquired, not by the capture of ions from the air, but by the ordinary frictional process involved in blowing the spray. If then ordinary static charges are built up of electrons, this charge should be found to be an exact multiple of the ionic charge which had been found from the most reliable measurement shown in Table I to be proportional to the velocity .00891. This initial charge e_n on the drop is seen from equations (9) and (10) to bear the same relation to $(v_1 + v_2)$ which the ionic charge $e_n' - e_n$ bears to $(v_2' - v_2)$. Now, $v_1 = .5222/13.595 = .03842$, hence $v_1 + v_2 = .03842 + .04196 = .08038$. Dividing this by 9 we obtain .008931, which is within about one-fifth of 1 per cent of the value found in the last column of Table I as the smallest charge carried by an ion. *Our experiment has then given us for the first time a means of comparing a frictional charge with the ionic charge, and the frictional charge has in this instance been found to contain exactly 9 electrons.* A more exact means of making this comparison will be given presently, but suffice it to say here that experiments like the foregoing have now been tried on thousands of drops in different media, some of the drops being made of non-conductors like oil, some of semi-conductors like glycerin, some of excellent metallic conductors like mercury. In every case, without a single exception, the initial charge placed upon the drop by the frictional process, and all of the dozen or more charges which have resulted from the capture by the drop of a larger or smaller number of ions, have been found to be exact multiples of the smallest charge caught from the air. Some of these drops have started with no charge at all, and one, two, three, four, five, and six elementary charges or electrons have been picked up. Others have started with seven or eight units, others with twenty, others with fifty, others with a hundred, others with a hundred and fifty elementary units, and have picked up in each case a dozen or two of elementary charges on either side of the starting-point, so that in all drops containing every possible number of electrons between one and one hundred and fifty have been observed and the number of electrons which each drop carried has been accurately counted by the method described. When the number is less than fifty there is not a whit more uncertainty about this count than there is in counting one's own fingers and toes. It is not found possible to determine with certainty the number of electrons in a charge containing more than one hundred or two hundred of them, for the simple reason that the method of measurement used fails to detect the difference between 200 and 201, that is, we cannot measure $v'_2 - v_2$ with an accuracy greater than one-half of 1 per cent. But it is quite inconceivable that large charges such as are dealt with in commercial applications of electricity can be built up in an essentially different way from that in which the small charges whose electrons we are able to count are found to be. Furthermore, since it has been definitely proved that an electrical current is nothing but the motion of an electrical charge over or through a conductor, it is evident that the experiments under consideration furnish not only the most direct and convincing of evidence that all electrical charges are built up out of these very units which we have been dealing with as individuals in these experiments, but that all electrical currents consist merely in the transport of these electrons through the conducting bodies.

"In order to show the beauty and precision with which these multiple relationships stand out in all experiments of this kind, a table corresponding to much more precise measurements than those given heretofore is here introduced (Table II). The time

TABLE II

t_g Sec.	t_F Sec.	$\frac{1}{t_F}$	$\left(\frac{1}{t'_F}-\frac{1}{t_F}\right)$	n'	$\frac{1}{n'}\left(\frac{1}{t'_F}-\frac{1}{t_F}\right)$	$\left(\frac{1}{t_g}+\frac{1}{t_F}\right)$	n	$\frac{1}{n}\left(\frac{1}{t_g}+\frac{1}{t_F}\right)$
11.848	80.708	.01236				.09655	18	.005366
11.890	22.366		.03234	6	.005390			
11.908	22.390	.04470				.12887	24	005371
11.904	22.368		.03751	7	.005358			
11.882	140.565	.007192	.005348	1	.005348	.09138	17	.005375
11.906	79.600	.01254				.09673	18	.005374
11.838	34.748		.01616	3	.005387			
11.816	34.762	.02870				.11289	21	.005376
11.776	34.846							
11.840	29.286	.03414				.11833	22	.005379
11.904	29.236		.026872	5	.005375			
11.870	137.308	.007268	.021572	4	.005393	.09146	17	.005380
11.952	34.638	.02884				.11303	21	.005382
11.860			.01623	3	.005410			
11.846	22.104	.04507				.12926	24	.005386
11.912	22.268		.04307	8	.005384			
11.910	500.1	.002000				.08619	16	.005387
11.918	19.704	.05079	.04879	9	.005421			
11.870	19.668		.03874	7	.005401	.13498	25	.005399
11.888	77.630	.01285				.09704	18	.005390
11.894	77.806		.01079	2	.005395	.10783	20	.005392
11.878	42.302	.02364						
11.880			Means		.005386			.005384

Duration of exp. = 45 min.
Plate distance = 16 mm.
Fall distance = 10.21 mm.
Initial volts = 5.088.8
Final volts = 5,081.2
Temperature = 22.82° C.

Pressure = 75.62 cm.
Oil density = .9199
Air viscosity = 1.824×10^{-7}
Radius (a) = .000276 cm.
$\frac{l}{a}$ = .034
Speed of fall = .08584 cm./sec.

$e_1 = 4.991 \times 10^{-10}$

of fall and rise shown in the first and second columns were taken with a Hipp chronoscope reading to one-thousandths of a second. The third column gives the reciprocals of these times. These are used in place of the velocities v_2 in the field, since distance of fall and rise is always the same. The fourth column gives the successive changes in speed due to the capture of ions. These also are expressed merely as time reciprocals. For reasons which will be explained in the next section, each one of these changes may correspond to the capture of not merely one but of several distinct ions. The numbers in the fifth column represent simply the small integer by which it is found that the numbers in the fourth column must be divided in order to obtain the numbers in the sixth column. These will be seen to be exactly alike within the limits of error of the experiment. The mean value at the bottom of the sixth column represents, then, the smallest charge ever caught from the air, that is, it is the elementary *ionic* charge. The seventh column gives the successive values of $v_1 + v_2$ expressed as reciprocal times. These numbers, then, represent the successive values of the *total* charge carried by the droplet. The eighth column gives the integers by which the numbers in the seventh column must be divided to obtain the numbers in the last column. These also will be seen to be invariable. The mean at the bottom of the last column represents, then, *the electrical unit out of which the frictional charge on the droplet was built up, and it is seen to be identical with the ionic charge represented by the number at the bottom of the sixth column.*

TABLE III

n	$4.917 \times n$	Observed Charge	n	$4.917 \times n$	Observed Charge
1	4.917	—	10	49.17	49.41
2	9.834	—	11	54.09	53.91
3	14.75	—	12	59.00	59.12
4	19.66	19.66	13	63.92	63.68
5	24.59	24.60	14	68.84	68.65
6	29.50	29.62	15	73.75	—
7	34.42	34.47	16	78.67	78.34
8	39.34	39.38	17	83.59	83.22
9	44.25	44.42	18	88.51	—

"It may be of interest to introduce one further table (Table III) arranged in a slightly different way to show how infallibly the atomic structure of electricity follows from experiments like those under consideration.

"In this table 4.917 is merely a number obtained precisely as above from the change in speed due to the capture of ions and one which is proportional in this experiment to the ionic charge. The column headed 4.917 × n contains simply the whole series of exact multiples of this number from 1 to 18. The column headed 'Observed Charge' gives the successive observed values of $(v_1 + v_2)$. It will be seen that during the time of observation, about four hours, this drop carried all possible multiples of the elementary charge from 4 to 18, save only 15. *No more exact or more consistent multiple relationship is found in the data which chemists have amassed on the combining powers of the elements and on which the atomic theory of matter rests than is found in the foregoing numbers.*

"Such tables as these—and scores of them could be given—place beyond all question the view that an electrical charge wherever it is found, whether on an insulator or a conductor, whether in electrolytes or in metals, has a definite granular structure, that it consists of an exact number of specks of electricity (electrons) all exactly alike, which in static phenomena are scattered over the surface of the charged body and in current phenomena are drifting along the conductor. Instead of giving up, as Maxwell thought we should some day do, the 'provisional hypothesis of molecular charges,' we find ourselves obliged to make all our interpretations of electrical phenomena, *metallic as well as electrolytic,* in terms of it."

THE EXACT EVALUATION OF e

Stokes' equation ought to begin to fail as soon as the inhomogeneities of the medium (*i.e.,* the distances between the molecules) become comparable with the dimensions of the drop, for the drop then can begin to fall freely through the holes of the medium, and thus increase its speed. This means that the observed speed of fall would be more and more in excess of that given by Stokes' formula, the smaller the drop became.

It was found [8] that the following corrected form of Stokes' equation was necessary:

$$v_1 = \frac{2}{9}\frac{ga^2}{\eta}(\sigma - \rho)\left(1 + A\frac{l}{a}\right) \tag{7}$$

where l is the mean free path of the air molecules, but e, A, and a are all unknown.

Hence if e is the true value of the electron and e_1, as before, the observed value, based on Stokes' formula, we have

$$e = \frac{e_1}{\left(1 + A\frac{l}{a}\right)} \tag{8}$$

"As a matter of fact the whole correction term, $A\frac{l}{a}$ is a small one, so that it is never necessary to make more than two approximations to obtain a with much more precision than is needed for the exact evaluation of e.

"As soon as e was fairly accurately known it became possible, as indicated above, to make a direct weighing of extraordinarily minute bodies with great certainty and with a very high degree of precision. For we have already shown experimentally that the equation

$$\frac{v_1}{v_2} = \frac{mg}{Fe_n - mg} \tag{9}$$

is a correct one and it involves no assumption whatever as to the shape, or size, or material of the particle. If we solve this equation for the weight mg of the particle we get

$$mg = Fe_n \cdot \frac{v_1}{v_1 + v_2} \tag{10}$$

In this equation e_n is known with the same precision as e, for we have learned how to count n. It will presently be shown that e is probably now known with an accuracy of one part in a thousand, hence mg can now be determined with the same accuracy for any body which can be charged up with a counted number n of electrons and then pulled up against gravity by a known electrical field, or, if preferred, simply balanced against gravity after the manner used in the water-drop experiment and also in part of the oil-drop work.* *This device is simply an electrical balance in place of a mechanical one, and it will weigh accurately and easily to one ten-billionth of a milligram.*

"Fifty years ago it was considered the triumph of the instrument-maker's art that a balance had been made so sensitive that one could weigh a piece of paper, then write his name with a hard pencil on the paper and determine the difference between the new weight and the old—that is, the weight of the name. This meant determining a weight as small as one-tenth or possibly one-hundredth of a milligram (a milligram is about 1/30,000 of an ounce). Some five years ago Ramsay and Spencer, in London, by constructing a balance entirely out of very fine quartz fibers and placing it in a vacuum, succeeded in weighing objects as small as one-millionth of a milligram, that is, they pushed the limit of the weighable down about ten thousand times. The work which we are now considering pushed it down at least ten thousand times farther and made it possible to weigh accurately bodies so small as not to be visible at all to the naked eye. For it is only necessary to float such a body in the air, render it visible by reflected light in an *ultramicroscope* arrangement of the sort we were using, charge it electrically by the capture of ions, count the number of electrons in its charge by the method described, and then vary the potential applied to the plates or the charge on the body until its weight is just balanced by the upward pull of the field. The weight of the body is then exactly equal to the product of the known charge by the strength of the electric field. We made all of our weighings of our drops and the determination of their radii in this way as soon as we had located e with a sufficient degree of precision to warrant it.† Indeed, even before e is very accurately known it is possible to use such a balance for a fairly accurate evaluation of the radius of a spherical drop. For when we replace m in (18) by $4/3ma^3(\sigma - \varrho)$ and solve for a we obtain

$$a = \sqrt[3]{\frac{3Fe_n}{4\pi g(\sigma - \varrho)} \frac{v_1}{v_1 + v_2}} \qquad (11)$$

The substitution in this equation of an approximately correct value of e yields a with an error but one-third as great as that contained in the assumed value of e, for a is seen from this equation to vary as the cube root of e. This is the method which, in view of the accurate evaluation of e, it is now desirable to use for the determination of the weight or dimensions of any minute body, for the method is quite independent of the nature of the body or of the medium in which it is immersed. Indeed, it constitutes as direct and certain a weighing of the body as though it were weighed on a mechanical balance."

THE EVALUATION OF e AND A

Equation 8 may be written in the form

$$e^{2/3}\left(1 + A\frac{l}{a}\right) = e_1^{2/3} \qquad (12)$$

Now in our corrected form of Stokes' equation (see Eq. 7) by plotting the observed values of e_1 as ordinates and the corresponding values of $\frac{l}{a}$ as abscissæ, we should get a straight line. That the corrected equation is adequate, is evidenced by the results of a study (covering 60 consecutive days) of 58 droplets.‡

The variation of $\frac{l}{a}$ was done experimentally in two ways: (1) by holding the pressure constant and choosing progressively smaller droplets; (2) by varying the pressure, to which the mean free path l is evidently inversely proportional. Both methods checked. They covered a thirty-fold variation in $\frac{l}{a}$, a seventeen-fold variation in the pressure p, and a variation in the number of electrons carried per drop from 1 to 136.

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* See *Phil. Mag.*, **19**, 216 (1910); **21**, 757 (1911).

† *Phys. Rev.*, **2**, 117 (1913). This paper was read before the Deutsche physikalische Gesellschaft in Berlin in June, 1912.

‡ First presented before the Deutsche Physikalische Gesellschaft, June, 1912; and later before the British Association at Dundee, in September, 1912.

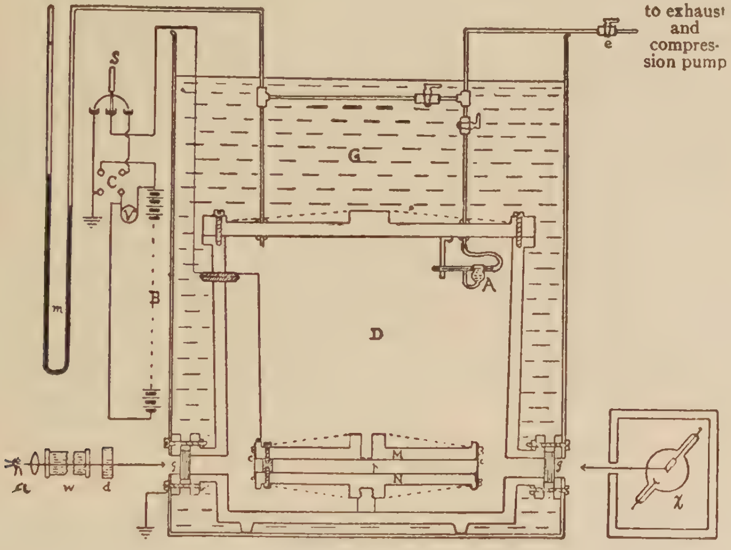

FIG. 1.

"The experimental arrangements are shown in Fig. 1. The brass vessel D was built for work at all pressures up to 15 atmospheres, but since the present observations have to do only with pressures from 76 cm. down, these were measured with a very carefully made mercury manometer m, which at atmospheric pressure gave precisely the same reading as a standard barometer. Complete stagnancy of the air between the condenser plates M and N was attained, first, by absorbing all of the heat rays from the arc a by means of a water cell w, 80 cm. long, and a cupric chloride cell d, and, secondly, by immersing the whole vessel D in a constant temperature bath G of gas-engine oil (40 liters), which permitted, in general, fluctuations of not more than .02° C. during an observation. This constant-temperature bath was found essential if such consistency of measurement as is shown here was to be obtained. A long search for causes of slight irregularity revealed nothing so important as this, and after the bath was installed all of the irregularities vanished. The atomizer A was blown by means of a puff of carefully dried and dust-free air introduced through cock e. The air about the drop p was ionized when desired, or electrons discharged directly from the drop, by means of Röntgen rays from X, which readily passed through the glass window g. To the three windows g (two only are shown) in the brass vessel D correspond, of course, three windows in the ebonite strip c, which encircles the condenser plates M and N. Through the third of these windows, set at an angle of about 28° from the line Xpa and in the same horizontal plane, the oil drop is observed through a short-focus telescope having a scale in the eyepiece to make possible the exact measurement of the speeds of the droplet-star.

"In plotting the actual observations I have used the reciprocal of the pressure $\frac{1}{p}$ in place of l, for the reason that l is a theoretical quantity which is necessarily proportional to $\frac{1}{p}$, while p is the quantity actually measured. This amounts to writing the correction-term to Stokes's Law in the form $\left(1+\frac{b}{pa}\right)$ instead of in the form $1 + A\frac{l}{a}$ and considering b the undetermined constant which is to be evaluated, as was A before, by dividing the slope of our line by its y-intercept."

Using a revised figure for η the coefficient of the viscosity of air $\eta = 0.0001824$ instead of 0.0001825, we find $e = 4.774 \times 10^{-10}$ electrostatic units.

"I have already indicated that as soon as e is known it becomes possible to find with the same precision which has been attained in its determination the exact number of molecules in a given weight of any substance, the absolute weight of any atom or molecule, the average kinetic energy of agitation of an atom or molecule at any temperature, and a considerable number of other important molecular and radioactive constants. In addition, it has recently been found that practically all of the important radiation constants like the wave-lengths of X-rays, Planck's h, the Stefan-Boltzmann constant σ, the Wien constant c_2, etc., depend for their most reliable evaluation upon the value of e. In a word, e is increasingly coming to be regarded, *not only as the most fundamental of physical or chemical constants, but also the one of most supreme importance for the solution of the numerical problems of modern physics.* It seemed worth while, therefore, to drive the method herewith developed for its determination to the limit of its possible precision."

After two years' work a still more accurate and delicate train of apparatus was developed, and with it in 1916 the value of e and N were fixed as follows:

$$e = 4.774 \pm .005 \times 10^{-10} \text{ electrostatic units}$$
$$N = 6.062 \pm .006 \times 10^{-10}$$

"Perhaps these numbers have little significance to the general reader who is familiar with no electrical units save those in which his monthly light bills are rendered. If these latter seem excessive, it may be cheering to reflect that the number of electrons contained in the quantity of electricity which courses every second through a common sixteen-candle-power electric-lamp filament, and for which we pay 1/100,000 of 1 cent, is so large that if all the two and one-half million inhabitants of Chicago were to begin to count out these electrons and were to keep on counting them out each at the rate of two a second, and if no one of them were ever to stop to eat, sleep, or die, it would take them just twenty thousand years to finish the task."

Brownian Movements in Gases

In 1827 the English botanist, Robert Brown,[9] first drew attention to the irregular wriggling motions exhibited by minute particles whose size approached the limits of resolvability in a high-power microscope. These Brownian motions, as they came to be called, strongly suggested "life"; but Brown showed that they also occurred with inanimate matter—pollen grains,* clay particles, etc.

Although many studied the phenomenon, it was not till half a century later that the Belgian Carbonelle first suggested that the cause of the Brownian motion was the continuous bombardment to which the particles were subjected by the molecules of the surrounding medium due to thermal agitation.†

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* The Brownian motion is not of the relatively large pollen grains themselves, but of tiny particles within them. J. A.

† Carbonelle's work was first published by his collaborator Thirion (*Rev. des questions scientifiques*, Louvrain, 7, 51 (1880); but three years before, Delsaulx, *ibid.*, 2, 319 (1877), in expressing this view had given due credit for priority to Carbonelle.

In 1881 Bordoszewski[10] saw in the Brownian motion of smoke particles *in air* "an approximate image of the movements of the gas molecules as postulated by the Kinetic theory of gases." During the next two decades, Gouy,[11] among others, urged the same interpretation, but an experimental test became possible only in 1905, through the brilliant theoretical work of Albert Einstein,[12] then at Bern, Switzerland.

> "Starting merely with the assumption that the mean kinetic energy of agitation of a particle suspended in a fluid medium must be the same as the mean kinetic energy of agitation of a gas molecule at the same temperature, Einstein developed by unimpeachable analysis an expression for the mean distance through which such a particle should drift in a given time through a given medium because of this motion of agitation. This distance could be directly observed and compared with the theoretical value. Thus, suppose one of the wiggling particles is observed in a microscope and its position noted on a scale in the eyepiece at a particular instant, then noted again at the end of τ (for example, 10) seconds, and the displacement Δx in that time along one particular axis recorded. Suppose a large number of such displacements Δx in intervals all of length τ are observed, each one of them squared, and the mean of these squares taken and denoted by $\overline{\Delta x^2}$: Einstein showed that the theoretical value of $\overline{\Delta x^2}$ should be
>
> $$\overline{\Delta x^2} = \frac{2RT}{NK}\tau \tag{13}$$
>
> in which R is the universal gas constant per gram molecule, namely, $831.5 \times 10^5 \frac{\text{ergs}}{\text{degrees}}$, T the temperature on the absolute scale, N the number of molecules in one gram molecule, and K a resistance factor depending upon the viscosity of the medium and the size of the drop, and representing the ratio between the force applied to the particle in any way and the velocity produced by that force. If Stokes' Law, namely, $F = 6\pi\eta a v$, held for the motion of the particle through the medium, then $K = \frac{F}{v}$ would have the value $6\pi\eta a$, so that Einstein's formula would become
>
> $$\overline{\Delta x^2} = \frac{RT}{N3\pi\eta a}\tau \tag{14}$$
>
> This was the form which Einstein originally gave to his equation, a very simple derivation of which has been given by Langevin.[13]

Perrin[14] made the first careful test of this equation on suspensions in liquids, and obtained for N a mean value of 68.2×10^{22}. Since his measurements vary as much as 30 per cent, and there are uncertainties in measuring both K and $\overline{\Delta x^2}$, these results may be considered as proving the correctness of Einstein's equation within the limits of the experimental error.

Although Bodoszewski (1881) had fully described and correctly interpreted Brownian movements in gases, no quantitative work on them appeared until 1909.*

Le duc de Broglie[15] now made an important advance. In March, 1908, he drew metallic dust (formed by striking an arc or sparking between metallic electrodes) † into a glass box and observing them through a microscope whose optical axis was set at right angles to the illuminating beam of light. This, essentially, was an ultramicroscope.

He passed the particles between two parallel vertical metallic plates, and observed on applying a potential difference to the plates, that some particles moved to one plate, some to the other, while some were unaffected; *i.e.*, there were positively and negatively charged particles.

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* Von Smoluchowski in 1906 (*Ann. der Phys.*, IV, 21, 756) had computed the mean displacements in air for particles with a radius of $a = 10^{-4}$ cm., and in 1907 Ehrenhaft (*Wiener Berichte*, II, **116**, 1175) had recorded displacements of the calculated order, without however measuring the sizes of the particles he used, so that the resistance factor K could not be computed and quantitative results obtained.

† Hemsalech and de Watteville (*Compt. rend.*, **144**, 1338 (1907)) had discovered this phenomenon; it recalls Bredig's method of obtaining colloidal dispersions by use of a metallic arc immersed in water, and Svedberg's later improvements.

In May, 1909,[16] he continued this work by studying the charges on minute droplets of water condensed on tobacco smoke.* He first observed the rate at which they moved in his horizontal electric field, the equation expressing their motion being

$$Fe = Kv \tag{15}$$

He next measured $\overline{\Delta x^2}$ for many particles and by introducing this into Einstein's equation

$$\overline{\Delta x^2} = \frac{2RT}{NK}\tau \tag{16}$$

he was able to eliminate K and obtain e in terms of N.

Using Perrin's value of N, de Broglie obtained from one series of measurements $e = 4.5 \times 10^{-10}$; another series on larger particles gave a mean value several times larger, which he interpreted as indicative of multiple charges on these particles.

Though these results give merely mean values for many drops not necessarily alike in radius or in charge, yet they may be considered to be the first experimental evidence that Einstein's equation holds approximately, for gases; and they are further significant because there has been no assumption as to the size or charge of the particles, or as to the validity of Stokes' law in gases, for the resistance factor K has been eliminated.

The development of the oil-drop method made it possible to subject the Brownian-movement theory to a more accurate and convincing experimental test than had heretofore been attainable, and that for the following reasons:

1. It made it possible to hold, with the aid of the vertical electrical field, one particular particle under observation for hours at a time and to measure as many displacements as desired on it alone instead of assuming the identity of a great number of particles, as had been done in the case of suspensions in liquids and in De Broglie's experiments in gases.
2. Liquids are very much less suited than are gases to convincing tests of any kinetic hypothesis, for the reason that prior to Brownian-movement work we had no satisfactory kinetic theory of liquids at all.
3. The absolute amounts of the displacements of a given particle in air are 8 times greater and in hydrogen 15 times greater than in water.
4. By reducing the pressure to low values the displacements can easily be made from 50 to 200 times greater in gases than in liquids.
5. The measurements can be made independently of the most troublesome and uncertain factor involved in Brownian-movement work in liquids, namely, the factor K, which contains the radius of the particle and the law governing its motion through the liquid.

Accordingly, there was begun in the Ryerson Laboratory, in 1910, a series of very careful experiments in Brownian movements in gases. Svedberg, in reviewing this subject in 1913, considers this "the only exact investigation of quantitative Brownian movements in gases." A brief summary of the method and results was published by the author. A full account was published by Mr. Harvey Fletcher in May, 1911, and further work on the variation of Brownian movements with pressure was presented by the author the year following. The essential contribution of this work as regards method consisted in the two following particulars:

1. By combining the characteristic and fully tested equation of the oil-drop method, namely,

$$e = \frac{mg}{Fv_1}(v_1 + v_2)_0 = \frac{K}{F}(v_1 + v_2)_0 \tag{17}$$

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* Zsigmondy had already made an ultramicroscopic examination of tobacco smoke. See "Zur Erkenntnis der Kolloide," 1904; or English translation by J. Alexander, "Colloids and the Ultramicroscope," 1909. J. A.

with the Einstein Brownian-movement equation, namely,

$$\overline{\Delta x^2} = \frac{2RT}{NK}\tau \tag{18}$$

it was possible to obtain the product Ne without any reference to the size of the particle or the resistance of the medium to its motion. This quantity could then be compared with the same product obtained with great precision from electrolysis. The experimental procedure consists in balancing a given droplet and measuring, as in any Brownian-movement work, the quantity $\overline{\Delta x^2}$, then unbalancing it and measuring F, v_1 and $(v_1+v_2)_0$; the combination of (17) and (18) then gives

$$\overline{\Delta x^2} = \frac{2RT}{F}\,\frac{(v_1+v_2)_0}{Ne} \tag{19}$$

Since it is awkward to square each displacement Δx before averaging, it is preferable to modify by substituting from the Maxwell distribution law, which holds for Brownian displacements as well as for molecular velocities, the relation

$$\overline{\Delta x} = \sqrt{\frac{2}{\pi}\,\overline{\Delta x^2}}\,.$$

We obtain thus

$$\overline{\Delta x} = \sqrt{\frac{4}{\pi}\,\frac{RT(v_1+v_2)_0}{F(Ne)}\,\tau} \tag{20}$$

or

$$Ne = \frac{4}{\pi}\,\frac{RT(v_1+v_2)_0\tau}{F(\overline{\Delta x})^2} \tag{21}$$

The possibility of thus eliminating the size of the particle and with it the resistance of the medium to its motion can be seen at once from the simple consideration that *so long as we are dealing with one and the same particle* the ratio K between the force acting and the velocity produced by it must be the same, whether the acting force is due to gravity or an electrical field, as in the oil-drop experiments, or to molecular impacts as in Brownian-movement work. De Broglie might have made such an elimination and calculation of Ne in his work, had his Brownian displacements and mobilities in electric fields been made on one and the same particle, but when the two sets of measurements are made on different particles, such elimination would involve the very uncertain assumption of identity of the particles in both charge and size. Although De Broglie did actually make this assumption, he did not treat his data in the manner indicated, and the first publication of this method of measuring Ne as well as the first actual determination was made in the papers mentioned above.

Some time later E. Weiss reported similar work to the Vienna Academy.[*]

2. Although it is possible to make the test of Ne in just the method described and although it was so made in the case of one or two drops, Mr. Fletcher worked out a more convenient method, which involves expressing the displacements Δx in terms of the fluctuations in the time required by the particle to fall a given distance and thus dispenses with the necessity of balancing the drop at all. I shall present another derivation which is very simple and yet of unquestionable validity.

In equation (21) let τ be the time required by the particle, if there were no Brownian movements, to fall between a series of equally spaced cross-hairs whose distance apart is d. In view of such movements the particle will have moved up or down a distance Δx in the time τ. Let us suppose this distance to be up. Then the actual time of fall will be $\tau + \Delta t$, in which Δt is now the time it takes the particle to fall the distance Δx. If now Δt is small in comparison with τ, that is, if Δx is small in comparison with d (say 1/10 or less), then we shall introduce a negligible error (of the order 1/100 at the most) if we assume that $\Delta x = v_1\Delta t$ in which v_1 is the mean velocity under gravity. Replacing then in (21) $(\overline{\Delta x})^2$ by $v_1^2(\overline{\Delta t})^2$, in which $(\overline{\Delta t})^2$ is the square of the average difference between an observed time of fall and the mean time of fall t_g, that is, the square of the average fluctuation in the time of fall through the distance *d*, we obtain after replacing the ideal time τ by the mean time t_g[1]

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[*] It was read before the Academy on July 6; *Wiener Berichte*, 120 (1911), II, 1021, but appeared first in print in the August 1st number of the *Phys. Zeitschr.* (1911), p. 63. Fletcher's article is found in brief in an earlier number of the same volume of the *Phys. Zeitschr.*, p. 203, and was printed in full in the July number of *Le Radium*, 8 (1911), 279.

$$Ne = \frac{4}{\pi}\frac{RT(v_1 + v_2)_0 t_g}{Fv_1^2(\overline{\Delta t})^2} \tag{22}$$

In any actual work $\overline{\Delta t}$ will be kept considerably less than 1/10 the mean time t_g if the irregularities due to the observer's errors are not to mask the irregularities due to the Brownian movements, so that (22) is sufficient for practically all working conditions.*

The work of Mr. Fletcher and of the author was done by both of the methods represented in equations (21) and (22). The 9 drops reported upon in Mr. Fletcher's paper in 1911 yielded the results shown below in which *n* is the number of displacements used in each case in determining $\overline{\Delta x}$ or $\overline{\Delta t}$.

TABLE IV

$\sqrt{Ne} \times 10^7$	n
1.68	125
1.67	136
1.645	321
1.695	202
1.73	171
1.65	200
1.66	84
1.785	411
1.65	85

When weights are assigned proportional to the number of observations taken, as shown in the last column of Table IV there results for the weighted mean value which represents an average of 1,735 displacements, $\sqrt{Ne} = 1.698 \times 10^7$ or $Ne = 2.88 \times 10^{14}$ *electrostatic units, as against* 2.896×10^{14}, the *value found in electrolysis.* The agreement between theory and experiment is then in this case about as good as one-half of 1 per cent, which is well within the limits of observational error.

This work seemed to demonstrate, with considerably greater precision than had been attained in earlier Brownian-movement work and with a minimum of assumptions, the correctness of the Einstein equation, which is in essence merely the assumption that a particle in a gas, no matter how big or how little it is or out of what it is made, is moving about with a mean translatory kinetic energy which is a universal constant dependent only on temperature. To show how well this conclusion has been established I shall refer briefly to a few later researches.

In 1914 Dr. Fletcher, assuming the value of *K* which I had published for oil drops moving through air, made new and improved Brownian-movement measurements in this medium and solved for *N* the original Einstein equation, which, when modified precisely as above by replacing $\overline{\Delta x^2}$ by $\frac{2}{\pi}(\overline{\Delta x})^2$ and $(\overline{\Delta x})^2 = v_1^2(\overline{\Delta t})^2$ becomes

$$N = \frac{4}{\pi}\frac{RTtg}{Kv_1^2(\overline{\Delta t})^2} \tag{23}$$

He took, all told, as many as 18,837 Δt's, not less than 5,900 on a single drop, and obtained $N = 60.3 \times 10^{22} \pm 1.2$. This cannot be regarded as an altogether independent determination of *N*, since it involves my value of K. Agreeing, however, as well as it does with my value of *N*, it does show with much conclusiveness that both Einstein's equation and my corrected form of Stokes's equation apply accurately to the motion of oil drops of the size here used, namely, those of radius from 2.79×10^{-5} cm. to 4.1×10^{-6} cm. (280-400 μμ).

In 1915 Mr. Carl Eyring tested by equation (22) the value of *Ne* on oil drops, of about the same size, in hydrogen and came out within .6 per cent of the value found in electrolysis, the probable error being, however, some 2 per cent.

Precisely similar tests on substances other than oils were made by Dr. E. Weiss and

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* No error is introduced here if, as assumed, $\overline{\Delta t}$ is small in comparison with t_g. However, for more rigorous equations see Fletcher, *Phys. Rev.*, IV (1914), 442; also Smoluchowski, *Phys. Zeitschr.*, XVI (1915), 321.

Dr. Karl Przibram. The former worked with silver particles only half as large as the oil particles mentioned above, namely, of radii between 1 and 2.3×10^{-6} cm. and obtained $Ne = 10.700$ electromagnetic units instead of 9,650, as in electrolysis. This is indeed 11 per cent too high, but the limits of error in Weiss's experiments were in his judgment quite as large as this. K. Przibram worked on suspensions in air of five or six different substances, the radii varying from 200 μμ to 600 μμ, and though his results varied among themselves by as much as 100 per cent, his mean value came within 6 per cent of 9,650. Both of the last two observers took too few displacements on a given drop to obtain a reliable mean displacement, but they used so many drops that their mean Ne still has some significance.

It would seem, therefore, that the validity of Einstein's Brownian-movement equation had been pretty thoroughly established in gases. In liquids too it has recently been subjected to much more precise test than had formerly been attained. Nordlund, in 1914, using minute mercury particles in water and assuming Stokes's Law of fall and Einstein's equations, obtained $N = 59.1 \times 10^{22}$. While in 1915 Westgren at Stockholm by a very large number of measurements on colloidal gold, silver, and selenium particles, of diameter from 65 μμ to 130 μμ (6.5 to 13×10^{-6} cm.), obtained a result which he thinks is correct to one-half of 1 per cent, this value is $N = 60.5 \times 10^{22} \pm .3 \times 10^{22}$, which agrees perfectly with the value which I obtained from the measurements on the isolation and measurement of the electron.

It has been because of such agreements as the foregoing that the last trace of opposition to the kinetic and atomic hypotheses of matter has disappeared from the scientific world.

Wilhelm Ostwald, a distinguished representative of a group who had, until quite recently, withheld their allegiance to these theories, was led to say in the preface of a new edition of his *Outlines of Chemistry:*

> "I am now convinced that we have recently become possessed of experimental evidence of the discrete or grained nature of matter for which the atomic hypothesis sought in vain for hundreds and thousands of years. The isolation and counting of gaseous ions on the one hand . . . and on the other the agreement of the Brownian movements with the requirements of the kinetic hypothesis . . . justify the most cautious scientist in now speaking of the experimental proof of the atomic theory of matter. The atomic hypothesis is thus raised to the position of a scientifically well-founded theory."

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13. *Compt. rend.*, 146, 530 (1908). An abstract of Langevin's derivation is given in Appendix C of "The Electron."
14. *Compt. rend.*, 147, 475, 530, 594 (1908); 152, 1380, 1569 (1911); see also Perrin, "Brownian Movements and Molecular Reality," English translation by Soddy, 1912.
15. *Compt. rend.*, 146, 624 (1908).
16. *Compt. rend.*, 148, 1316 (1909).

Prof. Millikan's work, done with ærosols, shows that in them the colloidal particles may acquire charges by taking and holding varying numbers of electrons. This raises the question whether an analogous series of phenomena may not exist in other colloidal dispersions. J. A.

Surface Energy And Surface Tension

By Prof. William D. Harkins,
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1. Introduction. Importance of Surfaces and Surface Energy

The importance of surface energy is best exhibited by highly disperse or colloidal systems. Such systems may indeed be defined in terms of surface energy. Thus a colloid is distinguished by the fact that the surface or interfacial energy has a value which is an appreciable fraction of the molecular energy of the dispersed phase. For example, if one cubic centimeter of water is sprayed into spherical droplets 0.01 μ (10^{-6} cm.) in diameter, the superficial area of the droplets is six million square centimeters. The free surface energy for this area at 20° would be two hundred eighteen million ergs or 10.5 calories provided the surface energy per unit area were the same as for a plane surface, while the total surface energy would be 16.6 calories or one third as much as the kinetic energy of vibration * of the molecules of water.

The importance of interfaces arises also from their abundance, due to the fact that most solids, including cast iron, steel, stone, etc., consist of small crystals, each of which has a surface. These exist around every minute cell in the plant or animal body, and also around the nucleus or nuclei of each cell, around the fibrils, nucleoli, chromosomes, and on both sides of each membrane. The examination under the microscope or ultramicroscope proves, too, that so-called homogeneous fluid systems, such as air, water, etc., actually contain an enormous number of minute surfaces.

Surfaces are prominent also in that they form the *outside* of every phase or particle. Thus if a thermometer is used to test the temperature of a liquid, its bulb must first be put through the surface. In vaporization every molecule must jump out from the surface, and the condensation of a vapor occurs upon a surface. If two particles unite, a part of their surface disappears, while if a particle divides, a new surface appears. Thus it is evident that surface energy is the most fundamental property which distinguishes colloids from other systems.

2. The Phenomenon of Surface Tension

It is commonly observed that water drops on a hot stove or very dry dust assume a spherical shape, which is the form assumed by a balloon surrounded by a uniform elastic membrane. This suggests that every liquid is surrounded by an elastic film, the tension of which causes the surface to contract to the smallest possible area for the volume of the liquid, provided other forces (such as gravitation) do not act to change the form.

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* This energy of vibration is calculated for water in the gaseous state with a molecular formula H_2O. It is usually supposed that water is an associated liquid, so the molecular kinetic energy in the liquid would be less than for the vapor. For spherical particles of one micron in diameter the total surface energy is a little more than 0.3 per cent of that of molecular vibration.

If a faucet with a narrow orifice is turned on very slightly, a drop may be seen to form, and hang for some time, after which it drops very suddenly. The drop is supported before it falls by the vertical component of the surface tension. If a capillary tube is dipped into water, the liquid inside the tube rises higher than that outside. Here, also, the film of liquid on the inside wall of the tube exerts an upward pull. If a camel's hair brush is dipped into water, the hairs remain spread apart as if they were dry and in the air, but when the wet brush is pulled out of the water, the pull of the surface tension of the water binds all of the hairs compactly together.

A soap film stretched on a wire frame such as that shown in Figure 1 has two surfaces. If the distance *CD* is one half a centimeter, then this lower wire is in contact with one half centimeter of the film or one centimeter of surface. The pull on the film as measured by the weight of the wire and the weights suspended from it at *W* gives the surface tension of the surface per unit length. This may be expressed in dynes. If the wire is pulled downward one centimeter, then the surface increase in area by one square centimeter, so the work done is force × area $= \gamma \times 1 = \gamma$ ergs. This energy may again appear as work when the film contracts to its original position, so it possesses the characteristics of free energy. Thus 72.8 dynes per centimeter is the surface tension of water at 20°, and 72.8 ergs per square centimeter is the free surface energy of water at this temperature.

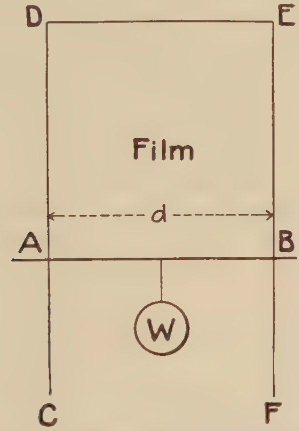

FIG. 1.—The Maxwell Frame. If the distance *AB* is one-half centimeter, the force *W* gives the surface tension of the soap film stretched on the frame.

3. TENSILE STRENGTH AND TENSILE ENERGY

There are a number of phenomena which indicate that the forces between adjacent molecules in solids and liquids are very high. Tensile strength tests on bars of steel show that it is necessary to apply a force[*] of 100,000

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[*] The energy used is unknown, since the distance through the force (*F*) acts is not known, and the energy (*E*) applied is given by the equation

$$E = \int_{s_i}^{s_f} F.ds \qquad (1)$$

in which s_i indicates the mean initial, distance between the molecules which are to be separated, and s_f is a distance so large that its further increase does not increase the energy appreciably. In addition to this an unknown amount of energy is used in deforming the bar before the break occurs.

pounds to rupture a bar one square inch in cross section. If it were possible to carry out a tensile strength test in an ideal way such that the bar (of 1 square centimeter cross section) would not be deformed before the break occurs, and so that the rupture would give two plane surfaces at right angles to the longitudinal axis of the bar, then the energy applied would be equal to twice the free surface energy (2γ) per square centimeter at the temperature of the test. This is true because *all that occurs in such an ideal rupture is the formation of a new surface* on the steel of 2 square centimeters area. This is equal numerically to twice the surface tension of steel per centimeter. The work necessary to thus pull apart a bar of unit cross section may be designated as the work of cohesion (W_c). Thus in the ideal case

$$W_c = 2\gamma \tag{2}$$

If an endeavor is made to apply such a tensile strength test to a bar of liquid, it is found that certain experimental difficulties arise. Nevertheless, the numerical value of the work of cohesion is known with considerable accuracy in such a case, since it may be obtained from the surface tension of the liquid. The surface tension of water at 20° is 72.80 dynes centimeter, so its work of cohesion is 145.60 ergs per square centimeter. This small value may seem to indicate a small tensile strength (force of cohesion) in water, but just the opposite is true since the distance to which molecular attraction remains appreciable is very small, and is only of the order of molecular dimensions. Furthermore, it decreases as a moderately high power of the distance. Suppose that the summation of this rapidly decreasing force is equivalent to the action of a constant force through 10^{-8} cm. Then the force of cohesion would be

$$\frac{145.6}{10^{-8}} \text{ or } 1.456 \times 10^{10} \text{ dynes} = 1.48 \times 10^{7} \text{ grams per square centimeter}$$

or about fourteen thousand atmospheres. The theory of van der Waals indicates a value of about 11,000 atmospheres, while other methods of calculation usually give between ten and fifteen thousand.

The difficulty in applying a tensile strength test to a bar of water arises from the fact that it is difficult to get hold of the ends, and even more to the fact that the break does not occur over the whole cross section of the bar at any instant. This is due, at least in part, to the presence of dissolved air and even more to minute bubbles of gas. That the tensile strength is of a considerable magnitude is shown by two types of experiments as described below.

If a plate of gypsum ($CaSO_4 . 2H_2O$) is sealed to one end of a long glass tube, the tube filled with air-free water and set upright with the open end in a trough of mercury and with the plate of gypsum at the top, it is found that water will evaporate through the gypsum, and the mercury will rise to four or five times the barometric height. This demonstrates that the cohesion in both the water and the mercury and also the adhesion between the two liquids is greater than five atmospheres.

In the second type of experiment a glass tube is sealed at the bottom and a moderately long open capillary tube is sealed on at the top. If the tube with its capillary are now entirely filled with air free water, the capillary may be sealed off below the surface of the water in the capillary. Thus the tube is left sealed and filled completely with water. Berthelot showed that if it is done with sufficient care the tube and its contents may be raised considerably without the water pulling away from the glass. Since the coefficient of expansion of water is considerably higher than that of glass, the water would be pulled away from the glass if it were not held by the effect of adhesion. Also the liquid itself would be pulled apart if it were not for the force of cohesion. Calculation showed that the pull of the glass upon the water amounted in some experiments to about 200 atmospheres.

4. Free and Total Surface Energy

The surface tension, and therefore the free surface energy, of a liquid decreases as the temperature rises, and very nearly as a linear function of the temperature. Thus the equation

$$\gamma = A + kT$$

which is that of a straight line, holds well over a moderate range of temperature (Fig. 2). A more exact equation for non-associated liquids is that of Ferguson [50] which has been shown by Sugden to hold remarkably well.

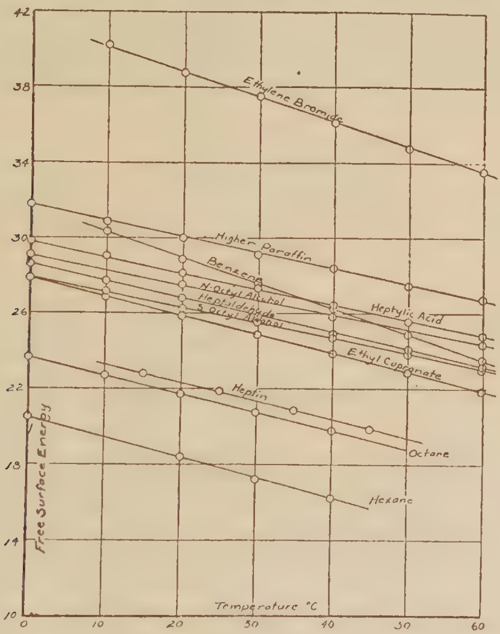


Fig. 2.—The surface tension of eleven pure liquids.

$$\gamma = \gamma_0 \left(1 - \frac{T}{T_c}\right)^{6/5} \qquad (3)$$

in which T_c is the critical temperature. The decrease in the surface tension of a liquid per degree of temperature is equal numerically to the *entropy* of the surface per unit area, and for unassociated organic liquids has a value of about 0.12 dyne per cm.

According to the rule of Le Chatelier, if the state of a system is changed, the system alters in such a way as to oppose a resistance to that change. Thus if the solubility of a salt increases with the temperature, the last amount of salt which dissolves to saturate the solution produces a cooling, since this cooling lowers the solubility, and thus opposes the solution of the salt. Now, since the surface tension decreases with the temperature, a surface must cool if it is expanded, since by cooling the surface tension is increased, and this opposes an extra resistance to the further extension.

That heat is used up in the formation of a surface is to be expected on other grounds. In the vaporization of a liquid the kinetic energy of molecular vibration of the molecules of the liquid, which determines the temperature, is partly converted into molecular potential energy. That is, the molecular energy of motion is utilized in the separation of each molecule from its neighbors and against the attraction which they exert. Now since a molecule which is in the interior of a liquid must move into the surface against the attraction of the surrounding molecules, as a part of its migration into the vapor phase, it seems probable that in surface formation as well as in vaporization, molecular kinetic energy would be utilized and transformed into potential energy of the surface. That heat is actually used in the formation of the surface is shown by the thermodynamic equation of Clapeyron; which gives the latent heat (1) of the surface as

$$l = -T\frac{\partial\gamma}{\partial T} \qquad (4)$$

The total energy (u) of a surface is equal to the sum of the free energy (γ) and the latent heat:

$$u = \gamma + l = \gamma - T\frac{\partial\gamma}{\partial T} \qquad (5)$$

For non-associated liquids equation 3 gives

$$u = \gamma_0\left(1+\frac{T}{5T_c}\right)\left(1-\frac{T}{T_c}\right)^{1/5} \qquad (6)$$

Thus, in the formation of a surface a part of the energy must be supplied in the form of work in order to give rise to the free surface energy, and a part comes from the kinetic energy which the molecules themselves possess. Thus if a person extends a surface by doing work upon it, the liquid will also contribute its share to the total energy. The Clapeyron equation tells us that the temperature, that is, the wealth of the molecules in kinetic energy, is an important factor in determining the extent of this contribution.

If a surface is to be formed on a definite liquid at a definite temperature, a definite amount of energy must be contributed and converted into potential energy. The writer has discussed this relation as applied to normal liquids as follows:[6]

The new principle or law will first be stated in one of its special forms as follows: *Whenever a molecule moves from the interior of a liquid into the surface* in such a way as to form a new surface, *the average amount of its kinetic energy which is converted into potential energy is equal to 144 per cent of the mean translational kinetic energy of a gas molecule at the same temperature.* This indicates that in general only the faster moving molecules possess sufficient kinetic energy to carry them into the surface. All known plane surfaces have a positive free surface energy, that is, the molecular potential energy in a plane surface in which the above principle holds, is always greater than 144 per cent of the mean kinetic energy of its molecules.

Application to the theory of surfaces.—As has been indicated in the last paragraph the molecules in a surface possess potential energy by virtue of their position. When a new surface is formed the principle given above indicates that a definite portion of this potential energy results from a transformation of the kinetic energy of molecular motion into the potential form, and that the amount of energy supplied in this form depends only upon the temperature; and is proportional to the temperature. *The free energy of the surface is simply the difference between the total energy, which depends upon the structure of the surface, and the latent heat of the surface which is conditioned by the above law.* It is easy to see why, on this basis, the surface tension or the free surface energy decreases rapidly with the temperature. The total surface energy is approximately constant (actually decreasing slowly) while the temperature is increased, provided the critical temperature is not too closely approached, which is the condition also for the application of the new principle since the surface film thickens as the critical temperature is neared. Since the contribution of the kinetic energy of molecular motion to this total energy is proportional to the absolute temperature, the free surface energy must decrease with the temperature.

5. The Entropy Relation

Extremely simple relations are exhibited by the entropy (S) of a surface, which is equal to the latent heat (l) divided by the temperature, or

$$S = \frac{\partial \gamma}{\partial T} \tag{7}$$

This gives the entropy per square centimeter, but a more simple function is obtained by calculating the entropy per area occupied by a single molecule, since this proves to be constant and equal to -3×10^{-16} ergs per degree for non-polar or non-associated organic substances, provided their molecules are not too large. Thus

$$s = \frac{\partial(\gamma v^{2/3})}{\partial T} = -2.96 \times 10^{-16} \text{ ergs} \tag{8}$$

per area of 1 molecule in the surface in which
v is the volume of a single molecule of the liquid, and is given by

$$v = \frac{M}{6.063 \times 10^{23} \, . \, d} \tag{9}$$

Thus the area used for a molecule in the surface is not the average area, which is often unknown, but simply the area of one face of a cube whose volume is the average volume occupied in the liquid by a molecule. Equation 8 holds only for symmetrical molecules.

The principle involved is expressed below in non-scientific or ordinary terminology. Whenever a molecule moves from inside a liquid into the surface region, a price in work must be paid from outside sources, but in addition the molecule itself must pay an entrance fee, which seems in terms of energy to be based upon an entirely socialistic principle. That is, the price paid in energy by the molecule is always proportional to the wealth of the molecule in translational kinetic energy at the temperature in question. Thus at 300° K (27° C.), the price paid is 8.9×10^{-14} ergs, while at 600° it is twice this, or 17.8×10^{-14} ergs.

In terms of entropy, however, the price paid by a molecule is the same $2.96 \times 10^{-16} \left(\frac{\text{erg}}{\text{degree}}\right)$, whatever the temperature.

It is evident that the above relation does not hold for a single molecule, but gives merely the average values. If the area taken for the calculation of the entropy is the face of a cube which contains a formula weight of the liquid, then the entropy is found to be 2.0 calories per degree. This is known as the constant of Eötvös. The experimental work of Ramsay and Shields showed that its value remains constant over a considerable range of temperature.

Concept of regions.—It is not sufficiently realized that the phase rule leaves out of account a type of portions of a system of supreme importance to the treatment of colloids. To avoid confusion the writer has applied to these the term *regions*. A phase, such as an aqueous phase, without any of the accompanying surfaces or interfaces, is termed a region, and each interface is also a region. Thus if a flask of water is suspended in air by an iron clamp, and if the clamp is left out of account, there are three phases: glass, water, and air (with vapor). Each of these without its interfaces against the others, is also a region. There are also three interfaces: glass-air, water-air, and glass-water, or in all there are three phasal regions and three interfacial regions, which give a total of six regions. If a fourth phase, hexane, is added, the number possible of regions is increased to ten, and with a fifth phase (solid) to fifteen.

Entropy of Vaporization.[7]

It is shown above that when a molecule, such as that of nitrogen or of a normal organic substance, passes from a liquid region into the liquid-vapor interface, it pays a constant price in terms of entropy, and this price is independent of the concentration of the vapor. Since in passing into the surface a molecule completes a certain section of its path into the vapor state, it is interesting to inquire if a somewhat similar entropy relation can be found for the process of vaporization. Now the Trouton relation as modified by Hildebrand may be stated: The price paid per molecule for passage from a liquid into a vapor region is constant in terms of entropy for any given concentration of vapor. Thus at 0.00507 mols/liter as the concentration of the vapor the entropy is 18.8×10^{-16} ergs per molecule, or 27.4 calories per mol. At 0.0201 mols per liter it is 15.7×10^{-16} ergs per molecule. The theoretical basis for the use of a constant concentration of vapor has been found by the writer to lie in the principle of equipartion of energy between (1) gaseous molecules of different masses at the same temperature, and (2) between molecules in the vapor and those in the liquid with which the vapor is in equilibrium.

6. The Second Law of Thermodynamics as a Special Exact Entropy Principle

In regional changes of any type in which molecules lose kinetic and gain potential energy, there is for any special type a more or less close adherence to the general principle that the molecules pay in terms of energy a price which is proportional to their mean wealth in kinetic energy at that temperature, which in turn is proportional to the temperature. The price depends, however, on the nature of the region from which the molecule emerges, and of that into which it passes, and does not take account of the energy used in connection with molecular association or dissociation. In the case of the conversion of heat into work, however, the conditions are more definite. Thus, if at a higher temperature the heat energy of a gas is converted into work, the amount of work produced is proportional to the temperature, and therefore to the mean kinetic energy of the molecules. Since the entropy is the energy divided by the temperature, the amount of entropy produced is independent of the temperature. Thus the price in energy paid by the molecules for the work done is proportional to the wealth in translational kinetic energy, but the price paid in terms of entropy is a constant.

The second law indicates that large molecules are no more effective than small ones in giving work at a specific temperature. Therefore, if all of the molecules in a certain mass of vapor were to associate themselves, so that three molecules would unite to form one, the work produced by an isothermal expansion (to the same relative extent) would be decreased to one-third the former value. If, now, the work were to be calculated on the basis of the molecular weight of the original gas, the calculated value would be three times larger than the amount of work actually obtained, and the actual entropy change would be also only one-third of that obtained by calculation. If the molecular entropy of formation of all surfaces were the same, as supposed by some workers who have treated the principle empirically, then it would be possible to determine the degree of molecular association in an exactly similar way. Thus if the entropy were only one-third of the standard value 2.0 calories per degree for the face of the molar cube, then on the average three molecules would have united themselves to form one.

However, there are several factors which make such assumptions of doubtful validity. First, the entropy of surface formation depends not only upon the kinetic energy of the molecules of the liquid with which the price is paid, but also upon the nature of the surface region into which admission is to be obtained. Second, a complicated molecule may vibrate not only as a whole, but also in parts, and it is not impossible that some of this latter kinetic energy may be utilized in surface formation as well as the translational energy. For example the molecule of tristearin is very large, and contains three hydrocarbon chains. If these three chains were three single molecules, each of which could move as a whole but not in parts, the molar entropy would be about 6 calories. Actually the entropy of tristearin is 5.55 calories per degree. Walden and Swinne have obtained an empirical expression for this entropy function (f).

$$f = -1.90 - 0.011 \Sigma A^{1/3} \tag{10}$$

in which A is the atomic weight of any atom. This equation has some value if used for such substances as nitrogen, oxygen, and organic substances, but in the case of mercury the nature of the surface is so different that the equation is not applicable. Thus the calculated value is 2.06, while the experimental value is 0.96. The equation is far from valid for highly polar substances. Thus for lithium chloride the equation gives 2.0, but experiment only one-fourth as much, 0.47 calories per degree.

7. An Electromagnetic Theory of Surfaces and Surface Energy

It may seem strange that a pull in the plane of a surface is used to bring molecules from below into the surface, for the surface tension has no component perpendicular to the surface plane. From the last section it is apparent, however, that if the surface molecules are pulled laterally from each other, those from below utilize their kinetic energy to carry them into the surface. Section 3 of this chapter shows the intimate relation between the cohesional work and the free surface energy. It is evident that the forces which give rise to the phenomenon of cohesion are just those which are causal for the related surface energy and tension.

There is definite evidence that an atom consists of a central nucleus, which contains nearly all of the mass of the atom. The nucleus is supposed to consist of a number, equal to the atomic weight, of hydrogen nuclei, bound together by about half as many negative electrons. Since the charge on each positive electron is equal to that on each negative electron, the net positive charge (Z) on the nucleus is equal to the number (P) of positive, minus the number (N) of negative, electrons, or

$$P - N = Z \tag{11}$$

which is also the atomic number of the element to which the atom belongs. Around the positive nucleus enough outer or planetary electrons are present to make the atom neutral, that is there are Z planetary electrons in any atom.

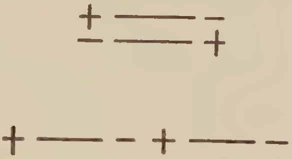


FIG. 3.—Electrical Couples.

One of the simplest of electrical principles is that like charges repel and unlike charges attract each other. If a positive and a negative electron could be placed so that they were coincident, then they would exert no electrical force on the exterior. It is known, too, that if the inner of two concentric spheres of conducting material carries a positive charge, and the outer an equal negative charge, there is no resultant electrical effect outside the latter. From this it might be supposed that if an atom, such as uranium which has 92 non-nuclear electrons, were to have these distributed on the surface of a sphere whose center is the nucleus, and as symmetrically as possible, then the electrical forces outside the atom would be relatively small. If the nucleus were in one position, and all of the negative planetary electrons in another, then the two would act as an electrical couple or bipole, and would either repel or attract other bipoles. However, if such couples are free to move it is found that they always arrange themselves so that the effect is an attraction. Two positions in which electrical couples attract each other, are shown in Fig. 3. Electrical theories of surface tension have been developed by J. J. Thomson,[8] Fraenkel,[9] and by Debye,[10] but the most complete theory is that of Fraenkel.

That the problem is not entirely one of electrostatics is indicated by the fact that substances exhibit magnetic as well as electrical characteristics. Electrons in motion produce an electromagnetic field, and the most successful atomic theory, that of Bohr, is based upon the concept that the electrons in the atom are in rapid motion. It seems therefore more general to consider that the attractive forces between atoms and those between molecules are electromagnetic, rather than simply electrostatic. At present, however, the electrical features of the theory have been much more highly developed than those concerning the magnetic relations.

The attractive forces between atoms of helium are exceedingly small. Thus helium atoms do not unite with each other to form diatomic molecules except for minute intervals of time, and then only when they are in an abnormal condition, when they are designated as "excited" atoms.

Helium exhibits all of the characteristics of a substance in which the cohesional forces are minute. Thus the boiling and melting points are very low (M. P. = 2° absolute), the surface tension of the liquid is very small, etc. The same may be said of all of the rare gases, neon, argon, krypton, and xenon. To explain these characteristics it is supposed that in the atoms of these substances the non-nuclear electrons are distributed in such a way as to exhibit a very high degree of symmetry. A helium atom has two non-nuclear electrons, a lithium atom three. This third electron acts as if placed far outside the two others in general, and the atom is not at all symmetrical. The melting point of lithium is 225 times higher than that of helium, so the cohesional forces are very much higher. It is considered that the four outer non-nuclear electrons of carbon are distributed with a high degree of symmetry, and it might be supposed from what has been given above, that the cohesion in carbon would be very low, but this is not at all the case, since the melting point of the diamond is extremely high (about 4000°), and the cohesion seems to be the highest of any known substance. Here a new factor enters, in that carbon atoms combine with other carbon atoms in what is considered a chemical union. This has been supposed by Stark and by Lewis to mean that adjacent atoms share pairs of electrons, so that there are four pairs of electrons around each carbon atom in a crystal of diamond. This pairing of electrons has not been explained, but suggests the action of other forces than those entirely electrical. Since gravitation is so minute as to be altogether insignificant, the only assumption left in the present state of our knowledge is that such effects are electromagnetic. The space lattice of carbon atoms in diamond is continuous. Each carbon atom is united to four others by "chemical" bonds, so all of the carbon atoms in a diamond crystal are in one chemical aggregate. Nevertheless such a crystal does not possess at all the distinctive characteristics of a molecule, since it is capable of indefinite extension without any decrease [11] in the inter-atomic forces. Contrast with this the case of chlorine. Each atom of chlorine is supposed to have seven electrons in its outermost or valence set of electrons. The affinity between chlorine atoms is very great. So to speak the cohesion of one chlorine atom for a second is extremely high. However, if two such atoms combine, presumably by sharing a pair of electrons, so that each of the two atoms is now surrounded by an octet of electrons, the attractive forces between any such pair of atoms and any other corresponding pair is low. Such a pair constitutes a true molecule. That is, a molecule consists of a set of atoms united in such a way that the forces which hold each atom in the set are high when compared with the forces between the sets when they are adjacent. Also with a molecule the set is complete, while in the case of a crystal it is never completed. Thus on the surface of chlorine the effective forces are those which are due to the completed sets, so the surface tension is low. On the surface of the diamond the electromagnetic field is the powerful one which gives rise to chemical combination, so the free surface energy of the diamond is extremely high.

It is supposed that the outer set of electrons is *complete,* in atoms of helium, neon, argon, krypton, and xenon. In the first of these the complete set consists of two electrons or a single pair. In all of the others it is supposed that four pairs constitute the set. As has been stated the surface tension of all of these substances in the liquid state is very low. The molecule of hydrogen contains a single pair of non-nuclear electrons, and this substance also has an extremely low surface tension. Nitrogen, in the molecules of which a set of ten electrons surrounds two *nitrogen* nuclei (each with its pair of inner planetary electrons), also has a very low surface tension. The highest surface tensions for the elements are found on the whole in the center of the periods in the periodic table, and the lowest surface tensions at the ends of the periods (Table I). Thus complete sets of outer electrons give the lowest tensions, half-complete sets the highest. When the sets are nearly complete, molecular formation occurs, and the surface tension of the *molecular* aggregate is moderately low. With elements at the beginning of the periods (after the first) the sets of electrons are less than half complete, so molecules do not form, and the surface tension is moderately high, increasing to very high as the set approaches half completion. With such atoms it seems that valence unions are possible on any side of the atom, and the electromagnetic stray field is very powerful outside the atom in any direction. In salts each ion has a complete set of outer electrons, which would indicate a low surface tension. However, each ion is charged electrically with a positive or a negative charge, so the electrical dipoles have a large moment, which causes the stray field and the resultant surface tension to be moderately high.

TABLE I

Periods and Cycles in the Periodic System of the Elements

	Cycle 1.	
Period 1.	First very short period	H — He = $2 = 2 \times 1^2$ elements.
	Cycle $2 = 4^2$ elements.	
Period 2.	First short period	Li — Ne = $8 = 2 \times 2^2$ elements.
Period 3.	Second short period	Na — A = $8 = 2 \times 2^2$ elements.
	Cycle $3 = 6^2$ elements.	
Period 4.	First long period	K — Kr = $18 = 2 \times 3^2$ elements.
Period 5.	Second long period	Rb — Xe = $18 = 2 \times 3^2$ elements.
	Cycle 4.	
Period 6.	First very long period	Cs — Nt = $32 = 2 \times 4^2$ elements.
Period 7.	....	Eka-Cs — U incomplete.

8. Cohesion and Distribution of a Solute between Regions

One of the important problems of colloids concerns the distribution of a solute between regions. This is the problem of adsorption. The present section gives an introduction to this subject by considering the subject of solubility, as presented in a former paper by the writer together with H. H. King.[11]

The first problem which will be considered is, given two components (A) and (B), each in a phase by itself, with both phases at the common temperature (T), when will these two phases be miscible, and when will they be practically insoluble in each other? Let (A) be in the liquid state. Then the relation is not difficult to find, for we know that (A) mixes with itself, so perfect miscibility should result when the stray fields around the molecules of (B) are sufficiently like those around those of (A). Likeness of fields in this sense means likeness in intensity, and presumably in the rate at which this intensity falls off with the distance from the molecule. A sufficient likeness of stray fields is also the condition which must hold if Raoult's law

$$p_A = P_A \frac{N_A}{N_A + N_B} = p_A x_A, \quad p_B = P_B \frac{N_B}{N_A + N_B} = P_B x_B$$

is to be valid. Here p_A and p_B are the vapor pressures of (A) and (B) over the mixture, P_A and P_B are the vapor pressures of the pure liquids, and x_A and x_B are the mol fractions of (A) and (B) in the mixture. If (A) is a liquid and if the stray field around the molecules of (B) is very nearly the same as that around the molecules of (A), then (B) will usually be a liquid also, if under the same pressure. The mass of the molecule, and its shape, are other factors which have some influence in this connection. If the stray fields around the molecules of (A) and (B) are sufficiently different in intensity, then the two substances will be practically insoluble in each other.

Since the intensity of the stray field falls off more rapidly with the distance around some molecules than around others, it is not possible to give a list arranged in order of increasing intensity of the stray field which is correct in all respects. Thus, while the intensity of the field close to the atoms of the heavy metals is very high, it undoubtedly decreases rapidly with the distance. On the other hand there are facts which seem to indicate that the forces around the oxygen or nitrogen atoms of organic compounds or of water, or such atoms as are commonly called "polar," extend to a greater distance, although their intensity is less at the ordinary atomic distances. However, the following list may be considered to give something of this order of increasing intensity for a limited number of substances. This list has been obtained for the most part from a consideration of the *surface-tension relations* of substances, and is as follows, beginning with those substances around whose molecules the stray field is weakest: helium, neon, hydrogen (molecular, not atomic), argon, krypton, xenon, nitrogen, oxygen, methane, carbon monoxide, and the following organic compounds: saturated aliphatic hydrocarbons, aromatic hydrocarbons, sulfides, mercaptans, halogen derivatives (methyl chloride, carbon tetrachloride, chloroform, and ethylene chloride, with rapidly increasing fields) unsaturated hydrocarbons, ethers, esters, nitro compounds, nitriles, aldehydes, ketones, alcohols, amines, acids, and unsaturated acids. Following these are water, molten salts, heavy metals, boron and carbon. The list of organic substances is arranged for derivatives with short hydrocarbon chains. A lengthening of the chain causes a displacement in the direction of lower intensity for polar derivatives, but probably toward higher intensity in the case of the hydrocarbons themselves. It will be seen that in general the greater the distance between the substances in this list, the less their solubility in each other, the closer together the more soluble. For organic substances, though the present list is much more extensive, it is in agreement with that found by Rothmund from solubility data.[58] It is well known that metals in general give concentrated solutions only with metals, carbon carbides (hydrogen), and other similar substances; molten salts dissolve salts or water; organic liquids are miscible unless at the very extremes of the list of organic substances; water dissolves salts or organic substances which are close to it in the list. An interesting illustration of this relation is given by data on the organic halogen derivatives listed above. The solubility of carbon tetrachloride per 1000 g. of water is 0.0052 mols, while that of chloroform which lies closer to water, is 0.068; and methylene chloride, approaching water still more closely, has a solubility of 0.236. This is also the order of increasing hydrogen content of the molecule, but that this is not the determining factor is indicated by the fact that methyl chloride and methane, similar compounds containing still more hydrogen, are much less soluble in water. In organic compounds the intensity of the stray field is much higher adjacent to what are commonly called double bonds, than it is near single bonds, and this intensity grows much larger still if triple bonds are introduced. Corresponding to this the solubility of ethane with its single bond between two carbon atoms, is 0.0507 volume of gas per volume of liquid; that of ethylene with its double bond is 0.1311, or more than twice as great, while acetylene with its triple bond has a solubility of 1.105, or about 22 times more than that of the single bonded compound.

In analyzing a solubility problem it is well to consider the attraction between the molecules of (A), between those of (B), and also that between (A) and (B). Consider octane and water which are mutually insoluble. It has sometimes been considered that this insolubility is due to the fact that water molecules attract each other more than they do molecules of octane, and that octane molecules attract each other more than they do molecules of water. Now the work of this laboratory shows that while the molecules of water do attract each other much more than those of octane, on the other hand the molecules of octane attract those of water no more than they do those of octane. The much greater attraction of the water molecules for each other is a sufficient cause to produce immiscibility, since it is only necessary that when a group of water molecules is once formed the mutual attraction shall be great enough to cause the molecules of water to leave the group less often than they enter it so long as there is an appreciable quantity of water in the octane. The octane molecules are thus left in a phase by themselves.

Since an increase in the intensity of the stray field around the molecule is accompanied by an increase in molecular attraction, it causes an increase in the cohesion of the liquid or of the solid, so in its application to pure liquids the above theory gives predictions which are similar to those obtained by that of Hildebrand,[46] that liquids of like cohesions are miscible, while those whose cohesions are very unlike are practically insoluble in each other. However, solubility is a molecular scale phenomenon, so there are certain advantages of a molecular theory. Moreover, the theory presented here has a much wider range of application, since it may be used to indicate the internal structure of a liquid, to predict the distribution of components between different phases, interfaces, and surfaces (these will be designated by the term *regions*), and is of great importance in theories of ideal and non-ideal solutions. In other words, it is a theory of what is called by Washburn[47] the *"thermodynamic environment."* This in the sense of our theory would be designated as the *electromagnetic environment.*

9. Polarity and the Electrical Moments of Molecules

If a body suspended upon an axis is acted upon by a force, the product of the magnitude of the force by the length of the lever arm is called the moment of the force. If a minute bar of length *l* has a positive charge equal to *ne* at one end and an equal negative charge at the other, the *electrical moment* of the bar is *lne*, or it is equal to the distance between the charges times the magnitude of the charge. The electrical moment of a molecule is defined in a similar way. Thus in a gaseous molecule of sodium chloride, the negative charge on the chlorine ion is equal to that of one electron, while the sodium ion has a positive charge of the same magnitude. If the electrons around the atom nucleus of each ion are distributed symmetrically, then the electronic center of gravity for each ion is coincident with its nucleus. The electrical moment of such a molecule is equal to the charge of an electron multiplied by the distance between the sodium nucleus and the chlorine nucleus. A molecule, such as that of sodium chloride, whose electrical moment is high, is called a *polar* molecule, and one with a moment so low as to be nearly zero, a non-polar molecule. Since the moment is probably never exactly zero, the term homo-polar is often used in place of non-polar to designate very low polarity. Helium, nitrogen, methane, hexane, and octane are examples of substances whose molecules have extremely small electrical moments, so they are commonly designated as non-polar.

If the material (dielectric) between the plates of a condenser is changed from a non-polar to a polar substance, it is found that with the same potential difference the charge held by the condenser is greatly increased. Thus it is 34 times larger with water than with hexane. However, a vacuum is taken as the standard of reference, and the dielectric constant of hexane is, on this basis, equal to 1.85, while that of water is 81. The capacity of the condenser is increased by polar molecules, since they rotate in the electrical field, the positive end of the dipole turning toward the negative plate, and the negative end toward the positive plate of the condenser.

Smythe[12] has recently calculated the molecular moment (μ) for a number of typical organic substances by the use of the theory of Gans. A few of the values are given in Table II. The calculation makes use of the dielectric constant, the index of refraction, the density, and the molecular diameter and weight for the substance in question.

TABLE II

MOLECULAR MOMENTS FOR WATER AND TYPICAL ORGANIC SUBSTANCES

	$\times 10^{18}$		
Water	1.98		
Paraffins		*Alcohols*	
Methane	<0.048	Methyl	1.78
Hexane	0.00	Ethyl	1.85
Octane	0.00	Propyl	1.98
Amylene	0.49	Butyl	2.06
Hexylene	0.28	Isobutyl	2.07
Octylene	0.50	Sec. butyl	1.95
Decylene	0.55	Tert. butyl	1.84
		Isoamyl	2.10
Ethers, etc.		*Amines*	
Methyl	1.37	Methyl	1.22
Ethyl	1.37	Trimethyl	0.86
Amyl	1.22+	Ethyl	1.26
Anisol	1.14	Di-isobutyl	0.98
H_2S	1.02	Aniline	1.30
C_2H_5SH	1.42		
$(C_2H_5)_2S$	1.58		

Halides

	Cl	Br	I
X_2	0.13	0.58	—
HX (liquid)	1.07	0.92	0.64
HX (gas)	1.03	0.79	0.36
CH_2X_2	1.73	—	—
CX_4	0.48	—	—
X_2CCX_2	0.45	—	—
CHX_2CHX_2	—	1.37	—
CH_2XCH_2X	1.55	1.07	—

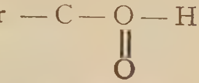
(Note: In general the values for polar molecules are too low, since the association is neglected.)

10. THE ORIENTATION OF MOLECULES IN SURFACES

A surface presents a most striking example of dissymmetry. On one side the electrical forces have an order of intensity similar to that in the interior of the liquid or solid, where they may give rise to a cohesion so high as to be equivalent to half a million megabars (or atmospheres), or to about seven and a half million pounds per sq. in. On the other side is a vapor, in which under ordinary conditions the molecules are so far apart as to produce only a negligible field between them. If a molecule with an appreciable electric moment enters the surface region where the electrical field has such a high order of dissymmetry, it seems evident that some degree of molecular orientation should ensue. The orientation would be lowered in degree, but not destroyed by the thermal agitation of the molecules. However, evidence is needed to show that the extent of the average orientation in the surface is sufficient to produce a noticeable effect in the characteristics of the region. Such evidence, of an altogether conclusive nature, has been supplied by the writer[13,14] and by Langmuir.[15]

The idea of orientation, but without evidence in its favor was presented by Hardy[16] in two interesting paragraphs, one published in 1912 and the other in 1913, as cited below.

> "The corpuscular theory of matter traces all material forces to the attraction or repulsion of foci of strain of two opposite types. All systems of these foci which have been considered would possess an unsymmetrical stray field—equipotential surfaces would not be disposed about the system in concentric shells. If the stray field of a molecule, that is, of a complex of these atomic systems, be unsymmetrical, the surface layer of fluids and solids, which are close-packed states of matter, must differ from the interior mass in the orientation of the axes of the fields with respect to the normal of the surface, and so form a skin on the surface of a pure substance having all the molecules oriented in the same way instead of purely in random ways. The result would be the polarisation of the surface, and the surface of two different fluids would attract or repel one another according to the sign of their surfaces." (Hardy, 1912.)
>
> "If the field of force about a molecule be not symmetrical, that is to say, if the equipotential surfaces do not form spheres about the centre of mass, the arrangement of the molecules of a pure fluid must be different at the surface from the purely random distribution which obtains on the average in the interior. The inwardly directed attractive force along the normal to the surface will orientate the molecules there. The surface film must therefore have a characteristic molecular architecture, and the condition of minimal potential involves two terms—one relating to the variation in density, the other to the orientation of the fields of force." (Hardy, 1913.)

These paragraphs were so well hidden that they would have remained unknown to the writer if he had not been incited to the search by a suggestion in regard to orientation which arose in his own mind in 1912. Prior to this time he had been engaged for several years in research on interfacial tension and solubility. In connection with investigations concerning the two phase system water-benzene the question arose as to the distribution of a polar-nonpolar molecule such as that of butyric acid. The solubility of this substance in (polar) water is due to the polar  $—C—\underset{\underset{O}{\|}}{O}—H$ or carboxyl group, and its solubility in (non-polar) benzene to the non-polar $CH_3CH_2CH_2$- or alkyl group. This is an illustration of the principle "like dissolves like." The solubility of the butyric acid in the polar phase is decreased by its hydrocarbon chain, and that in the non-polar phase by the carboxyl group. *At the interface, however, each end of the molecule can be in that phase in which it is most soluble: that is, the carboxyl group will dissolve in the water, and the hydrocarbon chain in the benzene. Thus the solubility of butyric acid should be greater at the interface than in either phase,* and that this is true is indicated by the fact that butyric acid greatly decreases the interfacial tension in such a system.

The principal attention of the laboratory became focused upon the evidence for orientation contained in data on the interfacial tension between pure liquids, and also between solutions, but, nevertheless it was natural that oil films on water should be considered to some extent. Thus a quotation from the lecture notes of George L. Clark, as taken during a lecture given by the writer in March, 1914, expresses tersely the fundamental basis of the entire theory in the statement "COOH of acid down because both acid and water associated and polar." The subject under discussion, as exhibited by the context, was the spreading of a film of oleic acid over the surface of water.

11. Direction of Orientation of Molecules as Exhibited by a Comparison of the Work of Adhesion with that of Cohesion

Data concerning the thickness of surface films on water give excellent evidence in favor of orientation, but they give no proof whatever as to whether the polar or the non-polar end of a molecule such as oleic acid is uppermost. The best evidence in favor of the fact that the polar groups turn toward the water, and the non-polar groups toward the air, is that obtained by a comparison of the work of adhesion of organic liquids against water or mercury, with the work of cohesion for organic liquids alone, and also by a comparison of the energy of surface formation with that of vaporization.

The logs which are seen floating upon the surface of the water of a river or lake are in a non-symmetrical field of force. They orient themselves with their longitudinal axis horizontal. If, however, each log is weighted with a mass of iron of the proper weight, it may still float, but the longitudinal axis becomes vertical (Fig. 4), the iron sinks below the surface, and the wood projects above it. In lectures this is easily illustrated by the use of a large glass trough of water upon the surface of which both weighted and non-weighted cylinders of wood are thrown. Cylinders one-eighth inch in diameter and four inches long are convenient since a very large number of them may be used to exhibit either the horizontal or the vertical type of orderly array.

The vertical type of orientation is due to the fact that the weighted end of each log is more highly attracted by the earth than the unweighted end. It may be assumed that the polar or carboxyl end of a molecule of butyric acid is more highly attracted by the liquid than the non-polar or hydro-

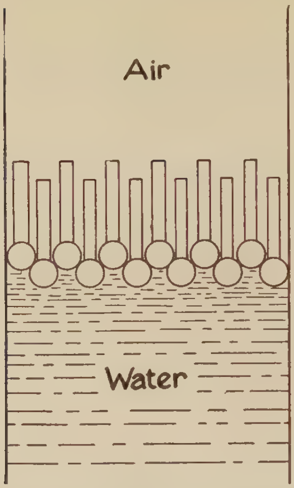


FIG. 4.—The orientation of weighted logs, or of polar-homopolar molecules, between water and air.

carbon end. That is, the polar end is more highly weighted than the other by electrical attraction.

If a bar of butyric acid or of octyl alcohol of unit cross section (Fig. 5) is pulled in two at the plane S, the molecules should first orient themselves on both sides of the plane where the break is about to occur. Fig. 6 indicates that the final work of separation will be affected most largely by the attractions between the non-polar ends of the alcohol molecules. However, in the first period of the separation *some* of the polar ends which are to go on

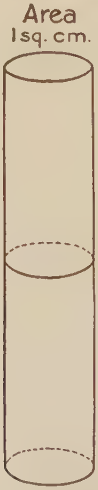


FIG. 5.—Cylinder of liquid with one square centimeter area of cross section. The work in ergs necessary to pull the liquid apart to form two plane surfaces perpendicular to the axis of the cylinder is equal numerically to twice the surface tension (2) in dynes.

the upper side of the plane must be separated from others which are to go to the lower side.* Thus it is to be expected that the work of separation of octyl alcohol from itself would be higher but not very greatly higher than the work of separation of octane from octane. So much for the theory. Let us see how the facts correspond. The work of cohesion (W_c) for octane is 43.5 ergs per sq. cm., or while, as indicated, that for octyl alcohol is moderately higher (55.1).

If, however, octyl alcohol is to be pulled away from water the relations are different. The hydroxyl groups should be turned toward the water, since polar groups are more highly attracted by a polar liquid, and the hydrocarbon groups of the surface film, away from the water (Fig. 7). *Here the final break must come between the polar hydroxyl groups of the alcohol and the water. Therefore the work of adhesion should be high.* The experiments of the writer and his associates indicate that this is the case, and that the value is 91.8 ergs per cm., or about 111 per cent higher than the work of separating the alcohol from itself.

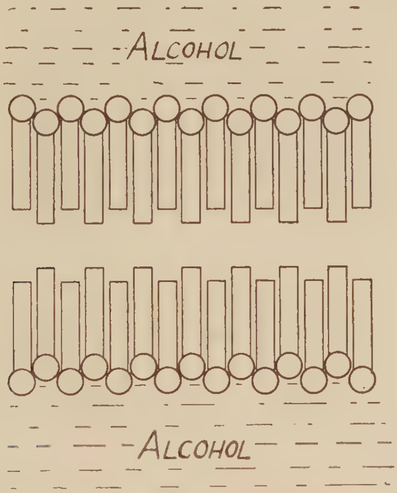


FIG. 6.—Orientation of alcohol molecules in the surfaces where a bar of liquid alcohol is pulled apart.

Since the work of cohesion for water is 145.8 ergs per cm., or higher than the work of adhesion between water and the alcohol, it might seem at first consideration that the hydroxyl groups of alcohol are not so highly attracted to water as might be expected, but it may easily be shown that this is not true. A plane water film would contain 10×10^{14} molecules per sq. cm. or the work of pulling water from itself is about 15×10^{-14} ergs per molecule. The work of pulling away the alcohol is twice as great, or 30×10^{-14} ergs per alcohol molecule if orientation is assumed (and even higher if there is no orientation), a value so high that it gives definite evidence that the hydroxyl groups are actually turned toward the water to a very considerable extent.

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* Also it is believed that polar characteristics transmit themselves, though in a highly reduced degree, along such a hydrocarbon chain.

It is of considerable interest that the work of pulling octane away from water is no larger than if octane is pulled from itself. Thus W_a is 43.8 for octane-water, and 43.5 for octane-octane, or the same within the limit of the experimental errors of the four determinations involved. *Thus the high polarity of the water is not effective in increasing the attraction for a non-polar liquid.*

A molecule of octane contains 26 atoms. The introduction of a single oxygen atom at the end of the chain converts it into octyl alcohol with a resultant increase in the cohesional work of 26 per cent. However, the adhesional work toward water is increased to a truly remarkable extent, by 111 per cent. The values for caprylic or capric acid are almost the same, and the relations between the values are similar for the amines and the nitriles and other compounds with highly polar groups at the end of a long chain. Thus it is evident that for non-symmetrical molecules such as octyl alcohol ($C_8H_{17}OH$), heptylic acid ($C_6H_{13}COOH$), and mercaptan (C_2H_5SH), the adhesional work (W_a) is determined by the strongest electromagnetic fields in the molecule, while the tensile work (W_c) is determined by the weakest fields, so for unsymmetrical molecules the work of adhesion is high, and the work of cohesion is low. In the case of entirely symmetrical molecules there

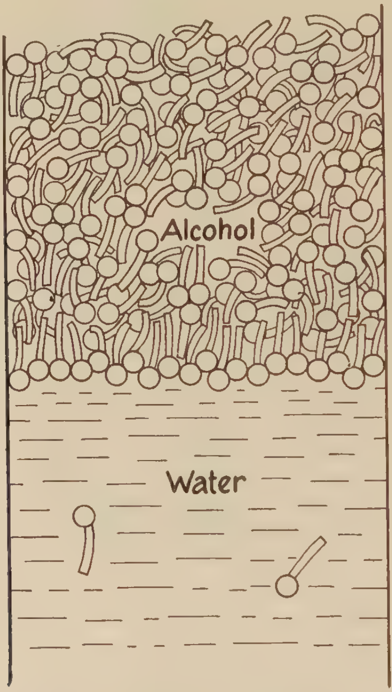

FIG. 7.—Orientation of alcohol molecules at the interface between alcohol and water. The orientation of the water molecules at the interface is not represented. It may be supposed that the liquid alcohol possesses a certain amount of structure or "association" (at any moment) due to the union of polar groups of the alcohol, or of polar groups of the alcohol with molecules of water dissolved in the alcohol if the latter is not dry.

could be no orientation. However, contrary to current opinion, the symmetry involved is not that of form, but is on the other hand largely that of the field around the molecule. The greatest problem in connection with the orientation theory is to determine the symmetry or lack of symmetry of the molecular fields of force. Fig. 8 represents a sphere, which, while entirely symmetrical with respect to its outer form, will orient itself with respect to a gravitational field, since it is heavily loaded on one side. A molecule which is quite symmetrical while in the vapor, may become much less so when it enters the non-uniform field at the surface of a liquid. *If a molecule increases its symmetry without a change of composition, the theory indicates that its cohesional work should increase, and its adhesional work toward water decrease, and the data indicate that this is true.* An increase of symmetry not

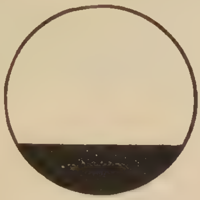

FIG. 8.—Weighted sphere oriented by gravitation. A molecule of high symmetry with respect to shape may be unsymmetrical with respect to the electromagnetic forces between it and surrounding molecules.

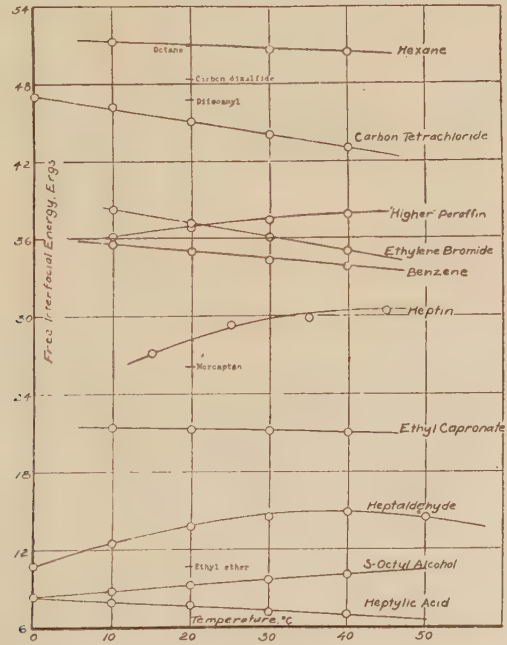

FIG. 9.—The free interfacial energy at phase boundaries between water and other liquids.

only reduces the extent of the orientation, but it also decreases the effect of the orientation upon the energy values involved.

Thus it is only when an organic molecule is at least moderately symmetrical with respect to its field, that the work of cohesion can become higher than that of adhesion. Thus $W_a - W_c$, which will be designated as the spreading coefficient S, is dependent upon lack of molecular symmetry for its high values, and upon the presence of such symmetry for high negative values. For the highly unsymmetrical alcohols and amines S is about 50, while for CS_2 it is -7, for tribromhydrin ($CH_2BrCHBrCH_2Br$) it is -11, and for acetylene tetrabromide ($Br_2CHCHBr_2$) it is -15.6. In general liquids will spread upon the surface of another liquid if the spreading coefficient of the former is positive, and will not spread if it is negative. *Thus the spreading coefficient for a substance upon water is a good indicator of the symmetry of the field of the molecules of the substance.*

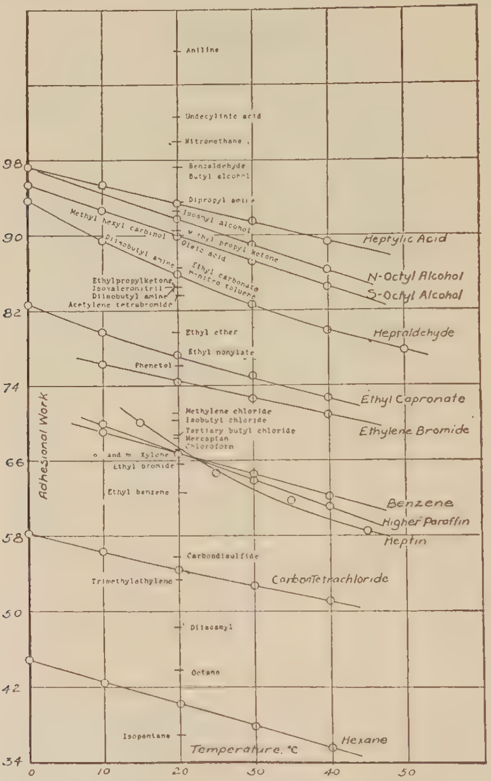

FIG. 10.—The adhesional work between water and other liquids.

A careful study of the energy values of Table III will show that their evidence in favor of molecular orientation in surfaces is convincing. Similar data for about 100 organic substances have been determined by the writer and his associates.[17] A few of these are represented in Figs. 9 and 10.

TABLE III

Illustrates the Small Effect on the Cohesional, and the Large Increase of the Adhesional Work Which Accompanies a Decrease in the Symmetry of Molecules of the Substance

(In the table the substance in the upper phase is listed above, and that in the lower phase, below the line. Energy values in ergs per sq. cm. of cross section of the bar of liquid disrupted.)

Octane	Octyl Alcohol	Octylene	Heptylic Acid	Heptane
43.5	55.1	44.7	56.6	40.2
Octane	Octyl Alcohol	Octylene	Heptylic Acid	Heptane
Octane	Octyl Alcohol	Octylene	Heptylic Acid	Heptane
43.8	91.8	72.9	94.8	41.9
Water	Water	Water	Water	Water

CCl_4	CCl_4	$(CH_3)_3CCl$	$(CH_3)_3CCl$
53.5	56.2	39.2	68.6
CCl_4	H_2O	$(CH_3)_3CCl$	H_2O
$CHCl_3$	$CHCl_3$	$(CH_3)_2CH_2CH_2Cl$	$(CH_3)_2CH_2CH_2Cl$
54.3	67.3	43.8	70.3
$CHCl_3$	H_2O	$(CH_3)_2CH_2CH_2Cl$	H_2O
CH_2Cl_2	CH_2Cl_2	$(CH_3)CH_2CH_2CH_2Cl$	$(CH_3)_2CH_2CH_2CH_2Cl$
53.0	71.0	47.0	80.8
CH_2Cl_2	H_2O	$(CH_3)CH_2CH_2CH_2Cl$	H_2O

CS_2	C_2H_5SH
62.8	43.6
CS_2	C_2H_5SH
CS_2	C_2H_5SH
55.8	68.5
H_2O	H_2O

A comparison of octane and octylene shows that the double bond in the latter increases the cohesional work only from 43.5 for the former to 44.7 for the latter, or a practically negligible increment. On the other hand, that a single double bond at the end of this molecule which consists of 24 atoms causes a high attraction for water as is shown by the increase of more than 66 per cent in the adhesional work. *Such a pronounced effect could not occur if orientation were absent.* It may be remembered that the molecular moment of octylene is only about one sixth that of the corresponding alcohol, so the high attraction between octylene and water as revealed by the high adhesional work suggests that the polarity of the double bond is increased by the proximity of the highly polar water at the interface.

The molecular moments of carbon tetrachloride, chloroform, and methylene chloride (CH_2Cl_2) increase in the order listed, being 0.48 for the first and 1.73 for the last, yet the cohesional work is almost the same: 53.5, 54.3, and 53.0. The effect of the increasing molecular moment is paralleled, however, in the increasing attraction for water, since the respective values of W_a are respectively 56.2, 67.3, and 71.0.

The above discussion relates to the work, which is the same as the free energy, of various surface changes. The *total energy* of these changes is even more important, but not so many values are known. All of the work done thus far upon this important problem is that of Harkins and Cheng.[18] They show that the values for the total energy exhibit exactly the same type of variation as that given above for the free energy values, and thus add another set of data which indicate molecular orientation in surfaces. The following paragraph is quoted from the summary of their paper.

> The addition of *one* oxygen atom to the *26* other atoms present in octane to give octyl alcohol increases the tensile *energy* by only 2 per cent, while it increases the adhesional *energy* by 65 per cent, and similar relations are found for the organic acids, aldehydes, and heptin. In contrast with this, it is found that the double bonds increase the tensile energy greatly, about 40 per cent, in the change from hexane to benzene, while the adhesional energy toward water is increased by only about 30 per cent. It is found, too, that the very symmetrical halogen derivatives, carbon tetrachloride and ethylene dibromide, which give *specially high values* for their own *tensile energy,* give *specially low values* for their adhesional energy toward water. The tensile energy of ethylene dibromide, on account of its symmetry, is higher than that of ethylidene bromide. These facts are easily explained on the basis of the hypothesis that the unsymmetrical molecules are oriented in the surface, and therefore give very strong evidence in favor of the orientation hypothesis. When a bar of heptin (or of an organic acid, alcohol, aldehyde, amine, etc.) is pulled apart, the break occurs where the electromagnetic field (largely electrical) and the resulting attraction is weakest, that is between the hydrocarbon chains, and in order that this may be the case the hydrocarbon chains turn into the nascent surface in the process of its formation. In the benzene the symmetry of the molecules is so great that the break must occur between certain of the unsaturated groups, that is where the intermolecular electromagnetic field is high. The fact that the adhesional energy of octane is so greatly increased by the addition of one oxygen atom to form octyl alcohol, indicates by similar reasoning that the oxygen atoms turn toward the water at their interface. Thus the *adhesional energy* toward water is determined by the *strongest electromagnetic fields* in the molecule, while the *tensile energy* is determined by the *weakest fields, provided the molecules are unsymmetrical.*

12. MOLECULAR ORIENTATION AND THE SURFACE AND INTERFACIAL ENERGY RELATIONS OF A METAL

The theory of lubrication * indicates that one of the most important characteristics of a lubricant is the extent to which it adheres to the surfaces which it lubricates. The surfaces most commonly used are those of metals. There is no known method of determining all of the values for a solid, but the relations for a liquid metal have been worked out carefully by Harkins, Grafton,[19] and Ewing.[20] The surface tension of mercury was obtained by determining the weight of a drop of mercury which falls into a high vacuum from

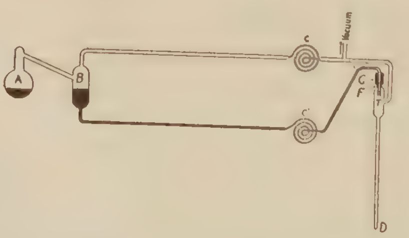

FIG. 11.—Flexible apparatus wholly of glass, for the determination of the surface tension of a liquid metal by the drop weight method.

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* See also paper by Sir W. B. Hardy, this volume. J. A.

a tip (*T*, Fig. 11) of an accurately known radius. The technique of the method is described below.

The mercury was purified by the methods recommended by the Bureau of Standards. It was then put into Flask *A*, after which the apparatus was sealed, dried, and evacuated by a mercury condensation pump. It was then distilled into reservoir *B*, with the pump still running. The spirals *C*, *C′* permitted the reservoir to be raised so that the mercury flowed over and dropped from the tip *T*. The height of *B* was adjusted so that a drop formed in 2 minutes. Determinations were made in which the time of formation of the drop was varied between one and five minutes and it was found that the weight of the drop is independent of the time whenever the period is greater than 1.5 minutes. When 10 drops had fallen into *D*, the tube was sealed off and another 10 drops collected. The sealed portions of the tube containing the mercury were broken and the mercury weighed in a weighing bottle. A constriction was made in the capillary tube at *E* to control the speed of drop formation. In the diagram *F* represents a ground glass joint and *G* a mercury seal. It was found necessary to have the portion of the capillary tube above the tip perfectly smooth and clean. Any roughness of the glass or the presence of a particle of dust caused the mercury column to break apart at that point, so that many tubes had to be tried before a satisfactory one was found. A 2-stage mercury condensation pump was used in producing the vacuum, and the system was evacuated for 2 hours before starting the collection of drops. The pressure was so low that no pressure could be detected by the use of a McLeod gage. The results obtained are given in Table IV. The surface tension, Col. 2, are calculated from the equation $\gamma = mg/2\pi\tau\psi(\tau/v^{1/3})$ and the latent heats from the Clapeyron equation $l = -T\Delta\gamma/\Delta T$.

The following results indicate that for mercury the Ramsay-Shields constant is 0.96 instead of the normal 2.12, or the entropy of surface formation for the area occupied by a molecule is 0.0135×10^{-14} ergs.

TABLE IV

THE FREE ENERGY, LATENT HEAT, AND TOTAL ENERGY OF SURFACE FORMATION OF MERCURY *in Vacuo*

(All values in ergs per sq. cm.)

Entropy of surface formation = 0.22 ergs per degree per cm.^{2}

1. Temp. ° C.	2. Free Energy of Surface Formation	3. Latent Heat of Surface Formation	4. Total Energy of Surface Formation	5. $\frac{\Delta\gamma/\Delta T}{\gamma_0}$
0	480.3	60.1	540.4	0.00046
10	478.3	62.3	540.6	—
20	476.1	64.5	540.6	—
30	474.2	66.7	540.9	—
40	471.3	68.9	540.2	—
50	469.4	71.1	540.5	—
60	467.1	73.3	540.4	—

At 20° the surface tension and free surface energy of mercury are represented by the number 476. If the other phase is water or an organic liquid instead of the vacuum, the free surface energy is decreased by from 86 to 172 ergs per sq. cm., the latter decrease being caused by methyl iodide whose surface tension is 35 dynes per cm. These values prove conclusively that the relation frequently cited, "the interfacial tension is the difference between the surface tensions of the two liquids," is very far from true. Thus 476 — 172 = 304 the actual interfacial tension, while 476 — 35 = 441, or a difference of 137 between fact and theory. Table V lists the surface and interfacial energy relations at constant temperature of mercury and various organic liquids.

TABLE V

The Adhesional Work Between Mercury, Water, and Organic Liquids, with the Cohesional Surface Work in Organic Substances for Comparison. (Liquids Arranged in Order of Adhesional Work Toward Mercury)

(In ergs per sq. cm.)

(1) Liquid	(2) Interfacial Tension Against Mercury	(3) Adhesional Work Against Mercury	(4) Cohesional Work Against Itself	(5) Difference (3) Minus (4)	(6) Adhesional Work Against Water	(7) Difference Mercury Minus Water (3-6)
(Air)	465	—	—	—	—	—
Hexane	378	120	36.9	83	40	80
Ethyl ether	379	123	43.6	79	73	50
Octane	375	127	43.5	83	44	83
Carbon tetrachloride	362	150	53.3	97	56	94
Chloroform	357	155	54.3	101	67	88
Benzene	363	146	57.6	88	67	79
Toluene	359	151	58.0	93	67	84
m-Xylene	357	152	58.0	94	64	88
o-Xylene	359	153	58.0	95	67	86
p-Xylene	361	155	54.0	101	64	91
Iso-butyl alcohol	348	155	45.6	109	94	61
Secondary octyl alcohol	348	159	—	—	—	—
Octyl alcohol	352	161	55.1	106	92	69
Methylene chloride	341	169	53.0	116	71	98
Ethylidene chloride	337	174	49.2	125	—	—
Nitrobenzene	350	173	86.8	86	91	82
Carbon bisulfide	336	175	62.8	113	56	119
Aniline	341	181	85.2	96	110	71
Water	375	182	145.6	36	145.6	36
Oleic acid	322	191	65.0	136	89.6	101
Ethyl iodide	322	195	56.4	139	63	132
Ethylene bromide	326	197	77.4	120	75	122
Methyl iodide	304	211	—	—	—	—
Acetylene tetrabromide	293	230	99.3	131	84	146
Mercury	—	960	960.0	—	182.6	(778)

Column 4 gives W_c, which is 2γ, for various organic liquids. Column 5 gives S, the spreading coefficient of various organic liquids on water. Note that all of the values are high and positive. See Section 15. The values of the adhesional work indicate that iodine or bromine atoms of an organic compound are oriented toward the mercury at the interface even more strongly than carboxyl groups.

13. Adsorption and the Distribution of a Substance between Regions

It has already been indicated (Sections 8 and 9) that the solubility of a substance and its adsorption in interfaces is highly dependent upon the electromagnetic fields of the various molecules.[11]

In studying this hypothesis the quantitative relations may be determined by the use of Gibbs' equation for adsorption.

$$\mu = -\frac{\partial\gamma}{(\partial F/\partial n)_A} = -\frac{1}{RT}\left(\frac{\partial\gamma}{\partial ln\, a}\right). \qquad (1)$$

Here μ gives the excess of solute in the surface film over that in the solution. F is the Gibbs' zeta function, a is the activity, and n represents the number of mols of solute. The equation may be expressed

$$\mu = -\frac{\partial\gamma/\partial r}{r\partial p/\partial r} \qquad (2)$$

where r is the dilution, and p is the osmotic pressure of the solution. For a perfect solution either of these reduces to

$$\mu = -\frac{1}{RT}\frac{\partial\gamma}{\partial lnc}. \qquad (3)$$

While in applying the hypothesis concerning the molecular fields the intensity of the stray fields around the molecules is of primary importance, at least one additional principle must be used if the direction which any change will take by itself is to be predicted. As might be expected the second law of thermodynamics is of fundamental importance in this connection, and for this purpose it may be stated in the form: Any change which takes place by itself in a system will proceed in the direction which will result in a decrease in the free energy of the system. Thus a surface will decrease in area by itself, but will not increase. Since a rapid variation of the intensity of the stray field with the distance in any direction, is accompanied by a high concentration of free energy, the second law indicates that in any change which takes place by itself, the variation in the stray field becomes less abrupt. If we imagine the surface of a liquid up to a bounding surface plane, to have just the same structure as the interior of the liquid, then the actual surface always has a smaller free energy than would be given by calculation for this imaginary surface, and therefore the drop in intensity of the stray electromagnetic field at the actual surface is always less than it would be at a surface of the structure of the imaginary surface. Since a molecule is often made up of several species of atoms, the stray field around it is often unsymmetrical. Thus many organic molecules, such as the primary normal alcohols, acids, amines, nitro compounds, nitriles, ethylene and acetylene derivatives, etc., consist of a paraffin chain, around which the stray field has a relatively low intensity (a so-called nonpolar group), while at the other end of the molecule there is a group containing oxygen or nitrogen, sometimes with metals in addition, around which the intensity of the stray field is relatively high (a polar group). Such molecules may be designated as *polar-nonpolar,* and designated by the symbol $\underset{\circ}{\square}$, where o represents the polar, and ▯ the nonpolar end of the molecule. If molecules of this type, such as butyric acid (C_3H_7COOH) are put in a two-phase system consisting of a polar liquid such as water, and a nonpolar liquid such as octane, then the free energy of the interface will be less when the transition from one liquid to the other is made by molecules of butyric acid, with their polar ends turned toward the water, and their nonpolar ends turned toward the octane, since in this way the abruptness of the transition is decreased.

The problem here arises as to the distribution of molecules of the polar-nonpolar type between the two liquid phases and the interface between them. It may be considered that each region (phase, surface, or interface) exerts a certain restraining force upon (has affinity for) the solute molecules. Since at equilibrium the thermodynamic potential of the solute is the same in all of the regions, it may be considered that the concentration of the solute (at equilibrium) in each phase, interface or surface, gives an index of the restraining force exerted by that region upon the solute molecules. Let us now assume that we have a number of exactly similar two-phase systems, each of which consists of equal volumes of a polar liquid, such as water, and a nonpolar liquid such as octane, with an interface of a definite area between them, and into each of these systems we put N molecules of the polar-nonpolar type $\underset{\circ}{\square}$. The hypothesis indicates that with a given polar group the distribution of the N molecules will vary in such a way that with an increase in the length of the nonpolar part of the molecule, the number of molecules, and therefore the restraining force in the octane will increase, while in the water both of these will decrease. The reverse of this occurs when with a given nonpolar chain, there is an increase in the number of polar groups. The greatest restraining force would be exerted on such molecules when they are in the interface, where the nonpolar end of the molecules could turn toward the nonpolar liquid, and the polar end toward the polar liquid. Since the restraining force is greatest at the interface, the concentration in this region should also be the greatest, which agrees with the facts as found by experiment. This case is more complicated than when the volume phases alone are considered, so it will be discussed in a later section.

In the general case, where a component (A) is distributed between a number of phases (a), (b), (c), etc., the distribution will take place in such a way that when equilibrium is obtained the highest concentration of (A) will be found in the phase between whose molecules (or atoms if there is no formation of molecular aggregates) the intensity of the forces (and probably the rate at which the intensity fall off with the distance) due to the electromagnetic field is most nearly similar to that around the molecules of (A). The least concentration of (A) will be found in the phase whose field is the most different from this, and in the other phases the concentration will increase as the properties of the phase approach those of (A) in the respect under consideration. The concentration in the various interfaces will be discussed in later paragraphs.

In the application of this very simple hypothesis certain complications must be kept in mind. The cohesion in nitrogen, for example, may be said to be due to the intermolecular field which is weak, and not to the interatomic field between the pairs of atoms, which is strong. In a like manner, if two butyric acid molecules unite to form a double molecule, the stray field is weakened, and the solubility in polar liquids such as water is greatly decreased, while that in slightly polar liquids such as octane, is greatly increased. The butyric acid is little associated in a dilute aqueous solution because most of its combinations will be made with the water (hydration) which is present in a much higher concentration than the acid. In extremely concentrated aqueous solutions, mostly butyric acid, the acid may be said to be associated to a considerable extent.

Relation at Surfaces and Interfaces.

While at the surface of a solid or liquid the amount of gas adsorbed at a given gas pressure increases in general both with the cohesion of the solid or liquid, and also with that in the liquefied gas, provided the surface is not saturated, there are exceptions to this rule which may be explained on the basis of electronic fittings. That the above rule is in general true is indicated by many facts: The adsorption on a mercury surface is much greater than that on a water surface in the case of the ordinary gases which do not react with either surface to form molecular aggregates; and the adsorption on a carbon surface increases with the boiling point of the adsorbed gas, etc. Thus the general case may be considered from the standpoint of cohesion (or adhesion) and deductions obtained which are in accord with the facts.

To a certain extent either of the above methods may be used to advantage at the interface between two liquids, but in some respects it seems simpler to use the hypothesis in regard to the intensity of the stray electromagnetic fields, although all 3 theoretical methods of consideration are related to each other. If two phases, (*A*) with the higher and (*B*) with the lower intensity of stray field uniting the molecules, could be put in contact in such a way as to have the field of each perfectly uniform up to a plane phase boundary or interface between them, then the whole drop in intensity between the two phases would occur in a surface of infinitesimal thickness; so, at least by certain methods of mathematical analysis, the free surface energy would be infinite. While this is not an actual case it suggests the idea that as the thickness of the transition layer increases the free surface energy diminishes. *With a given thickness of the surface layer* the free surface energy increases as the intensity of the stray field in (*B*) decreases, so the maximum free surface energy is reached when (*B*) is a vacuum, and is nearly realized when it is a dilute vapor or gas.

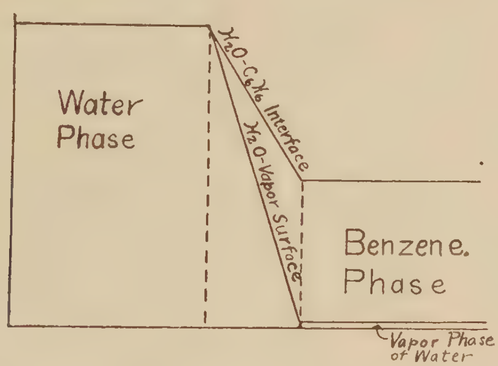

FIG. 12.—Drop in the intensity of the stray field between water and vapor, and between water and benzene.

In so far as the cohesion of a liquid is an index of the average intensity of the stray field in a liquid it might be expected that the free surface energy between the given liquid *A* and a fluid phase *B* would thus increase as the cohesion in *B* decreases, *provided the thickness of the surface film remains constant*. The values of the cohesion which should be used in such a comparison are not, however, those for pure liquids, but should be the results obtained for the saturated solution of each liquid in the other—if equilibrium values are desired. It is manifestly true that the equilibrium value of the interfacial free energy between miscible liquids is always zero.

Adsorption at Surfaces and Interfaces.

Consider a two-phase system which consists of water and water vapor, and a second system in which the vapor is replaced by benzene. As is indicated in Fig. 12 the intensity (Y-axis) of the intermolecular fields is greatest in water and least in the vapor phase of the water. Let butyric acid be added to both two-phase systems. The polar end of the butyric acid molecules is like water in the intensity of its stray field, and the intensity of the field decreases as the non-polar end of the molecule is approached. If these molecules enter the surface of the water or the interface between water and benzene, they make the drop in the intensity of the stray field perpendicular to the surface more gradual in both cases, and thus lessen the free energy. Since the free energy of the water surface is greater than that between the two liquids, the decrease in free energy is also greater, and the surface is a better trap than the interface for molecules of the polar-nonpolar type. Thus, since the drop in the intensity of the field is greater at the surface water-vapor than at the interface water-benzene, the restraining force is much greater in the former, and the average activity of molecules of butyric acid is much less in the surface than in the interface.

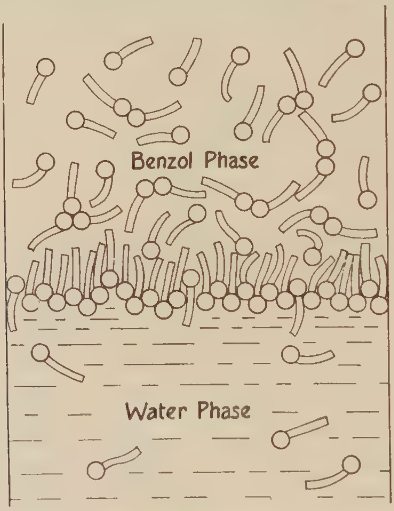

Fig. 13.—Distribution of butyric acid between water, the interface water-benzene, and benzene. The concentration of the butyric acid is highest in the interface. At high concentrations of butyric acid its concentration is higher in the benzene phase than in the water, but at low concentrations the concentration in the water is greater.

Experiments by Harkins and King[11] show that for a monomolecular film the activity of the butyric acid is 3.5 times greater in the interface than at the surface, entirely in accord with the conclusions of the last paragraph. It is further of interest that the number of molecules in the monomolecular film as calculated by the Gibbs' equation, was found to be 2.77×10^{14} per sq. cm. *whether the film is on the water surface or at the interface between water and benzene or between water and hexane,*[53] thus indicating this number to be dependent upon the area rather than the decrease in free energy involved.

Fig. 13 illustrates the distribution of butyric acid between butyric acid and benzol. Here the concentration is greatest at the interface, smaller in the benzol phase, and least in the water. In the benzol a part of the butyric acid is associated; that is, the carboxyl groups are together. Presumably this is a kinetic and not a static phenomenon. The relations may be explained qualitatively by assuming that associated butyric acid is more soluble in benzol than in water, and non-associated more soluble in water than in benzol. Since the association increases with the concentration, this agrees with the fact that at high concentrations more butyric acid is present in the benzol than in the water, while at low concentrations the reverse is true. Imagine a system water, surface, vapor in which the surface concentration of the butyric acid is the same as that of the interface of Fig. 13. Then the concentration of the butyric acid in the water is less than that illustrated in the figure, and is least of all in the vapor.

The Relation between Adsorption and Molecular Orientation.

The following discussion, taken largely from an early paper by the writer,[14] is included here in order to show that molecular orientation at the surface of a pure liquid, and the adsorption of molecules at the surface of a solution, are phenomena of essentially the same type. Thus molecular orientation consists merely in the adsorption in a surface of one end or side of a molecule in preference to the other. The end which is positively adsorbed is always the one which will give the lower surface tension, that is, the one which will make the work of forming the surface as small as possible. Thus in molecular orientation the outer surface takes that part of the molecule which may be raised into the surface with the least expenditure of work; in adsorption the surface takes those molecules which may be lifted into it most easily, and then of these the extreme outer part of the surface takes the ends which may be raised into it most easily.

Thus in molecular orientation the surface chooses those ends of the molecules which it can get by the least amount of work, and in adsorption it chooses the molecules which it can get by the least work.

1. The molecules in the surfaces of liquids seem to be oriented, and in such a way that the least active or least polar groups are oriented toward the vapor phase. The general law for surfaces seems to be as follows: *If we suppose the structure of the surface of a liquid to be at first the same as that of the interior of the liquid, then the actual surface is always formed by the orientation of the least active portion of the molecule toward the vapor phase,* AND AT ANY SURFACE OR INTERFACE THE CHANGE WHICH OCCURS IS SUCH AS TO MAKE THE TRANSITION TO THE ADJACENT PHASE LESS ABRUPT. This last statement expresses a general law, of which the adsorption law is only a special case. If the molecules are monatomic, and symmetrical, then the orientation will consist in a displacement of the electromagnetic fields of the atom. This molecular orientation sets up what is commonly called a "double electrical layer" at the surfaces of liquids and also of solids.

This law if applied to special cases indicates for a few pure liquids the following orientation: In water the hydrogen atoms turn toward the vapor phase and the oxygen atoms toward the liquid. With organic paraffin derivatives the CH_3 groups turn outward, and the more active groups, such as NO_2, CN, COOH, COOM, COOR, NH_2, $NHCH_3$, NCS, COR, CHO, I, OH, or groups which contain N, S, O, I, or double or triple bonds, turn toward the interior of the liquid.

If any of these organic compounds are dissolved in water, their orientation in the water surface is the same as that just given, with the active groups inward.

At interfaces between two pure liquids the molecules turn so that their *like* parts come together in conformity with the general law. With solutions, the solute molecules orient so that the ends of the molecules toward

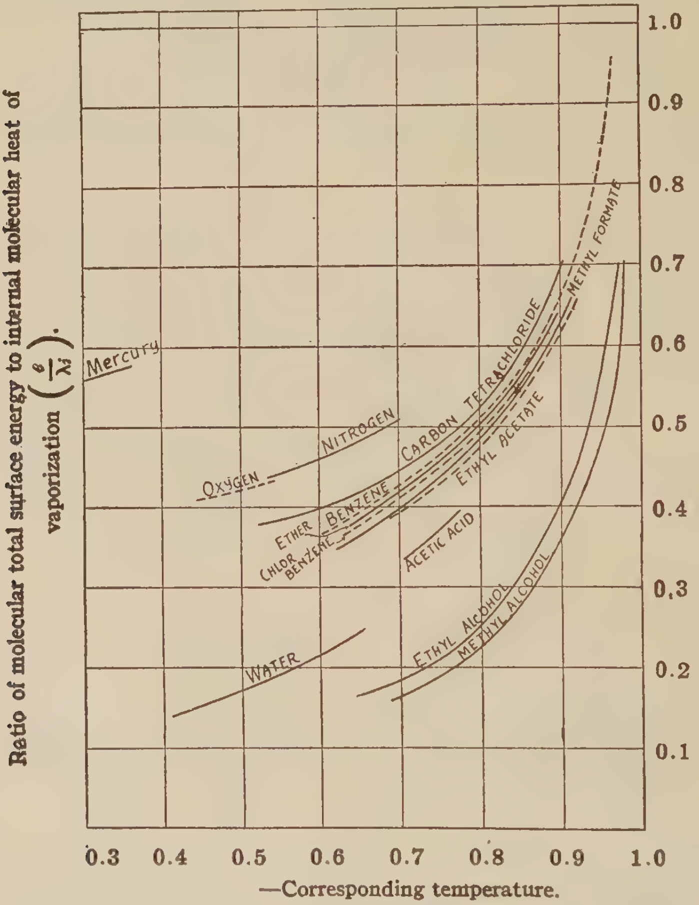

FIG. 14.—Ratio of the total surface energy to the latent heat of vaporization, per molecule.

the liquid *A* are as much like *A* as possible, and the ends toward *B* are as much like *B* as possible. So at interfaces between organic liquids and water, for example, the organic radical sets toward the organic liquid, and the polar group toward the water.

2. If at an interface the transition from a liquid *A* to the liquid *B* is made by a saturated film of solute molecules which we may call *A-B*, that is, they have one end like *A* and the other like *B*, then the free surface energy is greatly reduced. For example, with water and benzene with sodium oleate as the solute, the free energy falls as low as 2 ergs per cm^2.

3. If the solvent is polar, such as water, then solutes will in general be positively adsorbed in the surface if they are less polar than water, and the least polar end of the molecule will be turned outward. Solutes more polar than water are negatively adsorbed.

14. MOLECULAR ORIENTATION AS EXHIBITED BY THE RELATION BETWEEN THE ENERGY OF SURFACE FORMATION AND THE HEAT OF VAPORIZATION [7]

If a log weighted at one end by iron rests upon the bottom of a pond more shallow than the length of the log, the light or wooden end may be lifted to the surface of the water while the iron end still rests upon the bottom. However, if the log is to be lifted entirely out of the water the iron or heavy end must be lifted against the force of gravitation. The orientation theory supposes that in the processes of surface formation and of vaporization a molecule of the polar-nonpolar type acts in an entirely analogous way, since in surface formation it is mainly the nonpolar end which is raised into the surface, while in vaporization the polar or electromagnetically heavy end must be lifted entirely out of the liquid against the forces of molecular attraction. Thus the ratio of the total surface energy (u) to the internal latent heat of vaporization λ should not be very large. If the molecule is symmetrical there is no "lighter" end to be lifted into the surface so the surface energy should be more nearly of the same magnitude as that of vaporization. Thus the theory indicates that the ratio $\frac{u}{\lambda}$ should increase with an increase in the symmetry of the molecules.*

TABLE VI

LIQUIDS ARRANGED IN THE ORDER OF THE RATIO OF THE ENERGY NECESSARY TO CARRY A MOLECULE INTO THE SURFACE TO THAT REQUIRED FOR COMPLETE VAPORIZATION, AND PRESUMABLY IN ORDER OF INCREASING SYMMETRY IN THE SURFACE

(Corresponding Temperature = 0.7)

	Molecule	$\frac{u}{\lambda}$	$\frac{u}{j}$
	Class 1		
1.	Methyl alcohol	0.164	0.191
2.	Ethyl alcohol	0.186	0.228
	Class 2		
3.	Water	0.282	0.372
4.	Acetic acid	0.336	0.474
	Class 3		
5.	Ethyl acetate	0.397	0.606
6.	Methyl formate	0.402	0.618
7.	Chlorobenzene	0.417	0.714
8.	Ethyl ether	0.423	0.667
9.	Benzene	0.441	0.711
10.	Carbon tetrachloride	0.452	0.742
	Class 4		
11.	Oxygen	0.497	0.872
12.	Nitrogen	0.514	0.927
	Class 5		
13.	Mercury	0.636	1.41

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* The principal difficulty for an analogy between the action of gravitational forces upon the earth, and surface forces, lies in the extreme thinness of the layer, known as the surface, inside which the forces differ in magnitude. This is of the order of 1 $\mu\mu$ (or 10×10^{-8} cm.) in thickness.

As a molecule of the unsymmetrical type that of ethyl alcohol may be chosen, while that of carbon tetrachloride may be taken to represent symmetry. At a corresponding temperature of 0.7 only 0.19 as much energy is needed to carry a molecule of alcohol into the surface as to carry it completely into the vapor, while for carbon tetrachloride the corresponding value is 0.45; and at a temperature of 0.9, the numbers are 0.4 and 0.7; so in each case the value is very much lower for the unsymmetrical molecule, which is exactly what the theory predicts.

As might be expected, as the temperature rises the values for the unsymmetrical come closer and closer to those for the symmetrical molecules, since as the temperature rises the increase in the energy of vibration of the molecules tends to decrease the extent of the orientation.

These relations are shown plainly in Fig. 14 and Table VI.

15. Energy of Thermal Emission

The energy of thermal emission (j) for a molecule is the mean energy transformed in moving it from the surface into the vapor, and is thus the heat of vaporization minus the total surface energy, or

$$j = u - e$$

The value of the fraction $\frac{u}{j}$ is much more sensitive to changes of symmetry than that of $\frac{e}{\lambda}$. Thus at a corresponding temperature of 0.743 the energy of thermal emission for ethyl alcohol is four times that of surface formation, while for carbon tetrachloride the two have almost equal values. Table VII presents the values of γ, l, e, j, and λ, with calculated values in parentheses. The values calculated for ethyl alcohol from its critical temperature involve the assumption that its molecules are symmetrical, which is known to be untrue. This table and the discussion which follows it are taken from a paper by Harkins and Roberts.[7] The unit of energy used in the micri-erg, defined as 10^{-14} erg.

TABLE VII

Molecular Energy Values (in Micri-ergs) for the Vaporization of Liquids at a Corresponding Temperature Equal to 0.7

Liquid	T_c	γ	l	e	j	λ_i
1. Non-associated Molecular $= \mathfrak{T}$						
Nitrogen	127	1.51	2.33	3.84	4.8	8.7
Oxygen	154.2	2.24	2.26	4.50	6.1	10.8
Ethyl ether	467.5	4.0	11.7	15.6	20.9	36.5
(Ethyl acetate)	(524)	(4.6)	(13.7)	(18.3)	(27.7)	(46.0)
Carbon tetrachloride	556	4.7	13.5	18.2	22.0	40.2
Benzene	561.5	4.8	13.7	18.4	23.3	41.7
Chlorobenzene	633	5.3	15.0	20.3	28.5	48.8
2. Associated						
Methyl alcohol	513	2.8	5.7	8.5	43.1	51.6
Ethyl alcohol	516.1	3.5	7.7	11.2	48.1	59.3
		(4.4)	(12.5)	(16.9)	(20.4)	(37.3)

"The data indicate that *at a definite corresponding temperature, in the case of non-associated liquids whose molecules are symmetrical, the molecular values* *for the latent heat of surface formation* (l), *the total surface energy* (e), *the energy of thermal emission* (j), *and the internal latent heat of vaporization* (λ_i) *are nearly proportional to the critical temperatures of the liquids.* The same relation seems to hold for the free surface energy (γ) provided the temperature range is not too great. Thus the free surface energy of ethyl ether at a corresponding temperature of 0.7 is 4.0 as calculated from the value of carbon tetrachloride, and 3.9, as calculated from the value for chlorobenzene, while the experimental value is 4.0. This statement as applied to the latent heat of vaporization alone, is somewhat similar to Trouton's law, which is known to be not entirely exact. Since the principle expressed above is much more general in its application, it is to be expected that it will prove to be somewhat less exact. That the energy values for ether in Table VII are lower than those for carbon tetrachloride is related to the lower critical temperature of the ether.

"2. *The effect of a lack of symmetry in the molecule, especially when marked, is to lower the molecular free surface energy, latent heat of surface formation, and total surface energy, and to increase the energy of thermal emission.* The values given in parentheses under those for ethyl alcohol, are those calculated from the critical temperature under the assumption of a symmetrical molecule, using the values for carbon tetrachloride as a basis. It is evident that the molecular free surface energy, and total surface energy, and more markedly the latent heat of surface formation, are considerably lowered by the dissymmetry of the molecule. The most striking effect is, however, the very great increase in the energy of thermal emission. The symmetry referred to in this discussion is that of the electromagnetic forces around the molecule, rather than a symmetry with respect to mass. The substitution of the slightly polar chlorine atom for hydrogen in benzene gives almost exactly the calculated value for a symmetrical molecule except in the case of the thermal emission (j), which is considerably increased, since it is the most sensitive of all of the quantities to changes of molecular symmetry. Since u is decreased, and j increased by increasing dissymmetry of the molecule, the ratio $\frac{u}{j}$ serves as a remarkably sensitive index of molecular symmetry. This is illustrated in Table VI. The related ratio $\frac{u}{\lambda}$, which is equal to $\frac{u}{u+j}$, varies in the same way, but not so greatly.

"3. According to 'Stefan's law' the ratio of the total energy necessary to carry a molecule from the interior of a liquid into the surface to its total heat or energy of vaporization $\left(\frac{u}{\lambda}\right)$ is equal to ½. That this is not the case is easily seen by a reference to Table VII, and Fig. 14. Not only is this an increasing function with increasing symmetry of the molecule, but also with increasing corresponding temperature. Its value seems to approach unity as the corresponding temperature approaches unity. Thus a molecule in the surface at a high corresponding temperature is, in terms of relative energy, very much more nearly in the vapor phase than when the corresponding temperature is low.

"4. *The relations discussed in Paragraphs 1 and 2 above are just those indicated by the theory that molecules in the surface are oriented, the orientation increasing with increasing dissymmetry, and decreasing with increasing thermal agitation of the molecules.* The effect of thermal agitation is illustrated in the case of the alcohols; compounds of the polar-nonpolar type. Fig. 15 indicates that for these compounds the molecular surface energy increases with the temperature. The effect of increased agitation is partly to overcome the orientation and to throw the more polar groups into the outer surface, thus increasing the surface energy."

Fig. 15 gives the variation with the temperature of γ, *l*, *u*, and λ for mercury, water, and ethyl alcohol, and also for six "normal" liquids. The dotted lines give *j* for the alcohol.

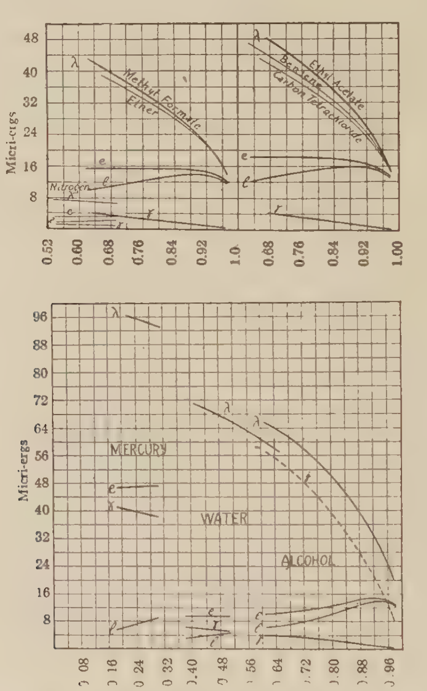


Fig. 15.—The molecular free surface energy (γ), latent heat of surface formation (*l*), total surface energy (*e*), latent heat of thermal emission of a molecule (*j*), and the internal latent heat of vaporization (λ). Where *j* is not given it may be obtained from the difference in height between the curves for *e* and for *l*.

16. The Spreading of Liquids ("Wetting Power")

Introduction

The spreading of liquids upon other liquids and the "wetting" of solids, are phenomena of great natural and industrial importance. The wetting of soils is fundamental not only to agriculture, but also to the existence of plant growth upon the soil. The process of washing with soap or without, in the household and in the industries, is also dependent upon wetting. The spreading of paint upon wood or metal, of tree sprays upon leaves, of a lubricating oil over the surfaces to be lubricated, of ink upon writing paper or upon the pages of books or newspapers, are all dependent upon this phenomenon. The water-proofing of fabrics by the use of aluminum stearate or other similar compounds depends upon the prevention of wetting. It is difficult for petroleum to penetrate sand impregnated with water, and "dry" wells, that is, those which no longer produce oil are often the result of the replacement of oil in the sand by water.

The process of mineral flotation, now used upon about 70 million tons of ore annually is dependent upon preferential wetting for its success. By its use sulfide ores may be separated from quartz or other gangue, lead and zinc sulfides may be separated from each other and from copper sulfide, bitumen from rock, coal from mineral matter, etc.

These facts incited Harkins and Feldman to a study of the scientific basis of this phenomenon, and a discussion of their work is presented in the paragraphs which follow.

Theories of Spreading.

Three different views of the criterion of spreading have been expressed in the literature. These are listed below.

1. All liquids spread on a pure surface.
2. A liquid b will spread on a liquid a if $T_a > T_b + T_{ab}$, where T_{ab} represents the interfacial tension between the two liquids, and T_a and T_b, the respective surface tensions. The condition for non-spreading is $T_a < T_b + T_{ab}$.
3. Liquids whose molecules are polar or contain polar groups, spread on water.

In addition to these a fourth view has been developed in this Laboratory.

4. A liquid will spread if its work of surface cohesion W_C is less, and will not spread if its work of surface cohesion is greater, than its work of adhesion W_A with respect to the surface of the liquid or solid upon which the spreading is to occur. The *spreading coefficient*, which under the conditions hereafter specified gives a measure of the tendency to spread, is defined as

$$S = W_A - W_C$$

The Neumann Triangle of Forces.

The second method of specifying the conditions for spreading, as listed above, was derived very early from a consideration of the Neumann triangle of forces. This assumes the surface tension of the under liquid to be pulling in one direction, and the surface tension of the upper liquid, together with that of the interface, to be pulling in the other direction. Motion of the edge of the drop takes place in the direction of the greater pull. Hardy, in his important work on composite surfaces, gives evidence for this idea as based on measurements with carbon tetrachloride, a paraffin oil, cyclohexane, and carbon disulfide.

Opposition to this point of view has been expressed by many workers in this field: Quincke,[2] Margaroni,[3] Worthington,[4] Rayleigh,[1] and others.

The Spreading Coefficient.

It would seem that the criterion for spreading might be expressed in a way much more easily justified theoretically if it could be developed entirely from the thermodynamics of surfaces. When a drop of liquid is placed upon the surface of another liquid a spreading may occur. If it does, the surface of the liquid a disappears, while its place is taken by substantially an equal area of the surface b plus an equal area of the interface ab, provided the surface of b and the interface ab do not lose their identity. If they do, then only one composite surface c takes the place of the surface a.

The spreading coefficient may be developed by thermodynamic reasoning, provided the former of the two hypotheses of the preceding paragraph is used as a basis. Since only large scale motion is of importance in spreading, only the *free* surface energies are involved. The free energy decrease S which occurs in spreading is obviously by the expression

$$S = \gamma_a - (\gamma_b + \gamma_{ab}) \tag{1}$$

where γ_{ab} represents the free energy of the surface or interface. The work of adhesion W_A, or the work necessary to pull apart the 1 sq. cm. of the interface ab, is given by the equation of Duprè as

$$W_A = \gamma_a + \gamma_b - \gamma_{ab} \tag{2}$$

since all that occurs is the disappearance of the surfaces a and b and the appearance of the interface ab. The work of cohesion is that necessary to create inside a liquid an area equal to 2 sq. cm., or more specifically to break apart a bar of liquid 1 sq. cm. in area in such a way as to give two surfaces, each 1 sq. cm. in area, and is given as

$$W_c = 2\gamma_b \qquad (3)$$

A combination of 1, 2, and 3, gives

$$S = W^A - W_c$$

which exhibits the extremely simple relation that spreading occurs if the adhesion between the 2 liquids is greater than the cohesion in the liquid which is in the position for spreading, while spreading does not occur if the cohesion is greater than the adhesion. It is obvious that a positive value of the spreading coefficient corresponds to spreading, a negative to non-spreading. It is also evident that because the liquid b spreads upon a, it is not at all a necessary conclusion that a spreads upon b. Thus the spreading coefficient is given above for the case where a is the liquid whose surface is already formed. The coefficient for a to spread upon b is $S = \gamma_b - (\gamma_a + \gamma_{ab})$ so a high surface energy for the liquid a acts in favor of spreading when a is the lower liquid, and against spreading when b is the lower liquid. *Corresponding with this it is found that almost all organic liquids spread upon water, while water spreads upon very few organic liquids.*

Definition of the Term "Film."

A definition of the term "film" which is suited to characterize films which exist upon liquids and solids, does not seem to have been given in any previous publication. A *film* exists wherever a layer, which has a different composition from the body of the liquid or solid, is present at the boundary surface, provided the area and form of this layer are independent of the gravitational forces acting. Whenever the area and the form of the layer depend upon both the surface and the gravitational forces, a lens *exists.* If the area and the form of the layer are determined primarily by the containing vessel, the phase may be said to be present in *bulk.*

Films may be said to be *non-composite* and *composite.* In a non-composite film the total surface energy is additive in that it is equal to the value of the interfacial energy when both phases are present in bulk, plus the value of the surface energy which film-forming material possesses when it exists in bulk in equilibrium with the phase upon which the film rests. In a composite film the total surface energy is less than this—so films may be very different in their degree of compositeness.

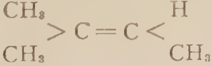
Since the distinction between a film and a lens, as given in the last paragraph, may not seem to be sufficiently definite, it will be given below in a slightly different form. The layer of liquid at a phase boundary may be considered to constitute a film whenever the gravitational forces which tend to change its form or area are inappreciable in comparison with the surface forces which are active.

The coefficients of spreading listed in Table VIII apply only to the spreading of the pure liquid upon an entirely clean water surface. If the surface of the water is impure, then the surface tension of the water, which occurs as a positive term in the spreading coefficient equation, is lowered, so the coefficient which should be used in this case has a lower value than the one given. Thus it has in no case been found that a pure liquid with a negative coefficient will spread, but it is often found in rough experiments that a liquid with a positive coefficient will not spread, due to the presence of a slight impurity on the surface of the water. As, organic liquids also, even when purified with great care, often differ slightly in their purity, the spreading coefficient relative to water should be determined by the use of a part of the same sample of liquid as was used in the spreading experiments. This was not done in the one exceptional case mentioned above, that of carbon tetrachloride, which has a very low positive coefficient relative to water of 1.06 dynes per cm., as determined by Harkins and Cheng. Unfortunately the liquid used in the determination of the coefficient was not available. It was found that, when the purest carbon tetrachloride which could be easily produced was put on a pure water surface, spreading did not occur. The spreading coefficient for this liquid has such a low value that it might be easily in error enough to account for such an exceptional result. Octane, with a still lower coefficient of only 0.22 dynes per cm., spread readily, while as stated above no liquid with a negative coefficient was found to spread.

TABLE VIII

The Spreading Coefficient of Organic Liquids on Water* at 20°

A. Spreading Liquids

Substance	Formula	S or $W_A - W_C$
Ethyl alcohol	C_2H_5OH	50.4
Methyl alcohol	CH_3OH	50.1
Propyl alcohol	C_3H_7OH	49.1
Dipropylamine	$(C_3H_7)_2NH$	48.60
Butyl alcohol	C_4H_9OH	48.30
Iso-butyl alcohol	$(CH_3)_2CHCH_2OH$	48.20
Propionic acid	C_2H_5COOH	45.77
Butyric acid	C_3H_7COOH	45.66
Ethyl ether	$(C_2H_5)_2O$	45.50
Acetic acid	CH_3COOH	45.20
Acetonitrile	CH_3CN	44.4
Iso-amyl alcohol	$(CH_3)_2CHCH_2CH_2OH$	44.3
Iso-valeric acid	$(CH_3)_2(CH_2)_2COOH$	43.89
Methyl ketone	$(CH_3)_2CO$	42.37
Di-*iso*butyl amine	$((CH_3)_2CHCH_2)_2NH$	40.47
Methylbutyl ketone	$CH_3COCH_2CH_2CH_2CH_3$	37.58
Sym-octyl alcohol	$CH_3OHC_6H_{13}$	37.32
Heptylic acid	$CH_3(CH_2)_5COOH$	37.12
Methylhexyl carbinol	$CH_3CHOH(CH_2)_5CH_3$	36.67
N-octyl alcohol	$C_8H_{17}OH$	35.74
Formic acid	$HCOOH$	35.5
Butyronitrile	$CH_3(CH_2)_2CN$	34.36
Iso-amyl chloride	$(CH_3)_2CHCH_2CH_2Cl$	33.88
Ethylpropyl ketone	$CH_3CH_2CO(CH_2)_2CH_3$	33.75
Ethyl carbonate	$(C_2H_5O)_2=C=O$	33.63
Iso-valeronitrile	$(CH_3)_2CHCH_2CN$	32.63
Heptaldehyde	$CH_3(CH_2)_5CHO$	32.22
Undecylenic acid (at 25°)	$C_{10}H_{21}COOH$	32.02
Methylhexyl ketone	$CH_3CO(CH_2)_5CH_3$	31.92
Ethyl *iso*-valerate	$(CH_3)_2CHCH_2COOC_2H_5$	30.71
Monochloro-acetone	$CH_2ClCOCH_3$	30.42
Tert-butyl chloride	$(CH_3)_3CCl$	29.46
Asym-dichloro-acetone	$CHCl_2COCH_3$	26.46
Iso-butyl chloride	$(CH_3)_2CHCH_2Cl$	26.43
Nitromethane	CH_3NO_2	26.32
Ethyl capronate	$CH_3(CH_2)_4COOC_2H_5$	25.64
Mercaptan	C_2H_5SH	24.86
Oleic acid	$C_{17}H_{33}COOH$	24.62
Iso-amyl butyrate	$(CH_3)_2CHCOO(CH_2)_2CH(CH_3)_2$	24.61
Aniline	$C_6H_5NH_2$	24.45
Heptine	$CH_3(CH_2)_4C \vdots CH$	22.40
Ethyl nonylate	$CH_3(CH_2)_7COOC_2H_5$	20.88
Trimethylethylene	 $\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!>C=C<\!\begin{matrix} H \\ CH_3 \end{matrix}$	18.85
Methylene chloride	CH_2Cl_2	17.97
Ethyl bromide	C_2H_5Br	17.44
Benzaldehyde	C_6H_5CHO	17.25
Iso-amyl nitrate	$C_5H_{11}NO_3$	14.82
Chloroform	$CHCl_3$	13.04
Anisole	$C_6H_5OCH_3$	11.76
Phenetole	$C_6H_5OC_2H_5$	10.66

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* The values of W_C from which the spreading coefficient were calculated relate to the pure dry organic liquids, but the latter in spreading become saturated with water, therefore still more exact information in regard to spreading would be given if W_C were determined by the use of liquids saturated with water.

TABLE VIII—*Continued*

Substance	Formula	S or $W_A - W_C$
p-Cymene	$C_6H_4CH_3C_3H_7$	10.10
Iso-pentane	$(CH_3)_2CHCH_2CH_3$	9.44
Benzene	C_6H_6	8.94
o-Xylene	$C_6H_4(CH_3)_2$	6.85
Toluene	$C_6H_5CH_3$	6.84
"Higher" paraffin		6.72
p-Xylene	$C_6H_4(CH_3)_2$	6.70
Tetrachloro-ethane		6.44
m-Xylene	$C_6H_4(CH_3)_2$	6.19
Ethyl benzene, mesitylene	$C_6H_3(CH_3)_3$	5.59
Trichloro-ethylene		5.09
o-Nitrotoluene	$C_6H_4CH_3NO_2$	4.15
m-Nitrotoluene		4.13
Nitrobenzene	$C_6H_5NO_2$	3.76
Di-*iso*-amyl (decane)	$(CH_3)_2CH(CH_2)_4CH(CH_3)_2$	3.76
Hexane	C_6H_{14}	3.41
Chlorobenzene	C_6H_5Cl	2.31
β,β′-dichloro-ethyl sulfide	$(ClCH_2CH_2)_2S$	1.62
Pentachloro-ethane		0.67
Octane	C_8H_{18}	0.22
B. Liquids which Form Lenses on Water		
Carbon tetrachloride		1.06(?)
p-Bromotoluene	$C_6H_5BrCH_3$	— 1.29(30°)
Ethylene dibromide	$C_2H_4Br_2$	— 3.19
Monobromobenzene	C_6H_5Br	— 3.29
o-Monobromotoluene	$C_6H_4CH_3Br$	— 4.20
Perchloro-ethylene	C_2Cl_4	— 6.42
Carbon disulfide	CS_2	— 6.94
Phenyl mustard oil	C_6H_5NCS	— 7.68
Monoiodobenzene	C_6H_5I	— 8.74
Bromoform	$CHBr_3$	— 9.58
α-Monochloro-naphthalene	$C_{10}H_7Cl$	— 9.74
Tribromohydrin	$CH_2BrCHBrCH_2Br$	—11.06
"Stanolax"		—13.44
Liquid petrolatum, Squibb's		—13.64
α-Monobromo-naphthalene	$C_{10}H_7Br$	—13.86
Acetylene tetrabromide	$C_2H_2Br_4$	—15.64
Methylene iodide	CH_2I_2	—26.46
Diphenyl methane	$(C_6H_5)_2CH_2$	
Diphenyl dichloromethane	$(C_6H_5)_2CCl_2$	
Tribromo-ethylene	C_2HBr_3	
p-Bromotoluene at 30°		— 1.29

Spreading as Related to the Presence of Polar Groups in the Molecule.

The 71 liquids listed in the first section of Table VIII were found by careful experiment to spread on the surface of pure water. These 71 liquids include hexane, octane, a higher paraffin, benzene, *iso*-pentane, toluene, *p*- and *m*-xylene, decane (di-*iso*-amyl), ethyl benzene, chlorobenzene, *iso*-butyl chloride, *tert*-butyl chloride, *iso*-amyl chloride; *a sufficient list to prove that the presence of a polar group is not essential for spreading.*

One of the principal effects of the presence of a polar group is, as has been shown frequently by Harkins and his co-workers, to increase the work of adhesion (W_A). Since when a very polar group, such as $-OH$, $-COOH$, $-CONH$, $-CHO$, $-CN$, $-CONH_2$, etc., is present, W_A is very high, the term W_C in the equation, $S = W_A - W_C$, is never large enough to give a negative value of the spreading coefficient. Nevertheless, when the work of adhesion toward water is small, the liquid may still spread if W_C is still smaller. Thus hexane, for which the value of W_A is very small (40.23 ergs), spreads, since W_C is extremely small (36.86), and the value of S is 3.37. The work of cohesion in octyl alcohol is nearly 20 ergs greater, so octyl alcohol is able to spread only because W_A is also greater (by the remarkably great value 51.71) than that for hexane. This illustrates the fact that the extremely great effect of the presence of a polar group in producing spreading is due to the fact that in general it increases the work of adhesion toward water very much more than it increases the work of cohesion.

Effect of Impurities on Spreading.

That impurities on the surface prevent spreading has been pointed out by many investigators; that active impurities in a non-spreading liquid, may cause it to spread, has been shown by Hardy[18] and others. A simple and beautiful experiment illustrates the latter effect. A large lens of "Liquid Petrolatum, Squibb"—presumably any other oil with a high negative coefficient would give similar effects—is formed in the middle of the surface of a sheet of water in a large tray. A drop of oleic acid is then placed upon the center of this lens. After a short period, considerable movement is noticed adjacent to this point and then, very suddenly, the lens is broken up into a great number of fragments which seem to be projected with almost explosive violence toward the edges of the tray. If the oleic acid is mixed with the oil before it is put on the surface, the material separates into a large number of minute drops, separated by a thin film, the drops moving constantly on the surface. The thin film evidently contains a considerable proportion of oleic acid.

Experiments on Camphorated Water.

The underlying idea of these experiments was to see to what extent spreading liquids could be made to stay in the form of lenses on water containing a substance in solution which lowers its surface tension. A lowering of the surface tension of water may affect the work of adhesion, $W_A = \gamma_{H_2O} + \gamma_{Liq} - \gamma_i$, in two ways: (1) by decreasing γ_{H_2O}; (2) by changing γ_i. The direction and magnitude of this last effect is difficult to predict. It was not determined experimentally, because in determining the interfacial tension of an organic liquid against a saturated solution of camphor, the camphor is so largely extracted by the organic phase. Judging from the spreading experiments, it seems that the effect of camphor on the work of adhesion consists chiefly in lowering the surface tension of water.

A saturated solution of camphor in water was made up, and its surface tension determined by the drop-weight method. The result varied somewhat between the limits 51.1 and 52.0; the lowering of the surface tension of the water is thus 21 ergs per cm.

Spreading experiments were made on this camphorated water following the same technique with respect to dusting and sweeping the surface, as was used with pure water. It was found that the following liquids did not spread on camphorated water: benzene, toluene, the 3 xylenes, mesitylene, nitrotoluene, chlorobenzene, anisole and benzaldehyde, whereas all of them spread on pure water.

The last 2 liquids are particularly interesting, since both contain polar groups having a high attraction for water. The spreading coefficient of benzaldehyde is given in the table as 17.25; this makes it probable that the main effect of camphor on the work of adhesion is in lowering the surface tension of water. It was also found that dimethylaniline, a substance with a polar group, did not spread on camphorated water. Nitromethane spreads on camphorated water as one would expect from the magnitude of its spreading coefficient on pure water, 26.32. The behavior of organic liquids on the surfaces of aqueous solutions is a subject of considerable interest and deserves further study.

Experiments on Mercury Surfaces.

A recent paper from this Laboratory[19, 20] gave a table of results of interfacial measurements on systems made up of mercury in contact with organic liquids. The column marked S or $W_A - W_C$ shows that the *spreading coefficient is positive in all cases.* It was, therefore, inferred that all these liquids should spread on a perfectly clean mercury surface.

Spreading experiments were made to test this hypothesis. The following liquids were tried and found to spread on mercury: (1) acetone, (2) hexane, (3) ethyl ether, (4) octane, (5) propyl alcohol, (6) nitro-ethane, (7) ethyl alcohol, (8) carbon tetrachloride, (9) toluene, (10) benzene, (11) *o*-xylene, (12) *m*-xylene, (13) *p*-xylene, (14) chloroform, (15) octyl alcohol, (16) nitrobenzene, (17) aniline, (18) water, (19) oleic acid, (20) ethylene bromide, (21) methyl iodide, (22) acetylene tetrabromide.

There are several interesting phenomena to note in connection with these experiments; liquids which do not spread on water, such as carbon tetrachloride, ethylene dibromide or acetylene tetrabromide, nevertheless spread on mercury.

In the case of water, Rayleigh's technique was followed:[22] mercury was distilled in a vacuum in an all-glass apparatus. A Drechsel wash-bottle attached as a receiver was later cut off from the distilling train, and the mercury used for the experiments siphoned from under the surface. This resulted, as described by Rayleigh, in an exceptionally clean mercury surface. Whether water will spread on such a surface or not depends further on the quality of the water used in the experiments. The quality of the water is probably responsible for the variable success which Rayleigh had with this experiment. Water spread on mercury may be found after a time gathered into a lens, which effect is probably caused by a contamination picked up by the mercury surface.

This experiment was formerly considered of great significance, since it was thought that this was representative of all cases of non-spreading liquids; their non-spreading on water, for example being supposed to be caused by the impure surface of the water. A consideration of the table quoted above shows, however, that if the spreading coefficient is a true criterion of spreading or non-spreading, water should spread on a mercury surface. Now water, of all liquids studied by Harkins, Ewing and Grafton, has the lowest spreading coefficient, so it is readily understood why great precautions must be taken in using both a clean mercury surface and pure water. Since a mercury surface is easily contaminated, the value of the spreading coefficient of water on an impure mercury surface can readily become negative and as a result water easily forms lens on a mercury surface. The conclusion is, therefore, that the behavior of mercury towards water represents nothing exceptional.

The same method of siphoning the mercury from under the surface was used not only for the experiments with water but also with the organic liquids. A few cubic centimeters of mercury which had been in the delivery tube and had perhaps adsorbed gases, was discarded in every experiment. The spreading of these liquids on mercury always takes place much more slowly than the spreading of the same liquid on water, even although the spreading coefficient is usually much higher in the former case. This illustrates the fact so well known with respect to other phenomena, that the free energy of a change and its speed are by no means proportional to each other.

The Non-spreading of Water on Organic Liquids.

While most organic liquids spread on water and have a positive spreading coefficient, the value of the latter is always negative, at least in every case thus far investigated. Thus it is to be expected that *water will in no case spread upon the surface of any organic liquid when the two are mutually insoluble.* It has already been seen that the spreading coefficients given in the table are calculated from data obtained from the pure liquids, and are not strictly applicable unless this condition is met by the lower phase and the film.

Corresponding with this, water was found to spread upon only 1 of the 18 organic liquids investigated, and this one, acetone, is miscible with water.

The form of the lenses produced by organic liquids on water has not been treated in this paper, since Coghill and Anderson have made a study of this subject. The general form of the drops of water which float on the surface of an organic liquid is very different, and does not seem to have been described.

A non-spreading organic liquid will form a lens on water, though sometimes only a very small one if the spreading coefficient has a low numerical value. This lens will always float if it is not too large, since it is upheld by the vertical component of the surface tension of the water at the line of contact. The floating of the lens depends upon the important fact that in no case does the water spread over the surface of the lens. If it did so, then the vertical component of the surface tension of the water would pull the lens downward instead of upward, and it would sink if its density were greater than that of water.

If we now consider what occurs when a *drop of water* is placed upon the surface of an organic liquid with which it is not miscible, it will be seen that since most organic liquids spread on the surface of water, the usual behavior is that described in the following sentences. The organic liquid spreads as a film over the drop of water, and the latter then sinks if it is heavier than the former, but, if it is lighter, *floats as a practically spherical lens or a globule such as is illustrated in Fig. 30. The surface of the organic liquid rises as it approaches such a floating lens*, while the surface of water always falls as it approaches a floating lens consisting of an organic liquid.

The phenomena which accompany the floating of a lens of water upon the surface of a non-spreading organic liquid should be similar to those which occur when a lens consisting of an organic substance floats upon water, but with this important difference: the surface tension of an organic liquid is so small in general that only a very small lens of water can be supported, provided the density of the latter is considerably greater than that of the organic liquid.

The non-spreading of water upon insoluble organic liquids is in good accord with the spreading coefficient relation.

The Spreading of Films on Solids.

Since the free surface energy of almost all inorganic solids is high, their work of cohesion is high, and the work of adhesion is also high with reference to practically all liquid substances. Since the work of cohesion in water and organic liquids is in general low, the values of the coefficient of spreading of these liquids upon such solids should be positive, and in general their values should be high. Thus the spreading of these liquids should occur upon such solids when their surfaces are pure. The frequently occurring phenomenon of non-spreading is thus indicated to be due to the presence of an already existent film upon the solid substance. The removal of such films may be brought about by vaporization, or by the more common process of substituting one film for another. This is the ordinary function of soap, soap solutions, and other cleansing agents.

17. MONOMOLECULAR FILMS AND MOLECULAR ORIENTATION

That certain liquids spread out into a film one molecule thick on the surface of water was indicated by Rayleigh[23] in 1899, and more definitely by Devaux,[24] who began his researches on this subject in 1903. In 1891 Miss A. Pockels[25] showed that if a very small amount of olive oil is put upon the surface of water in a trough, and the film compressed by movable barriers, the surface tension begins to decrease rapidly after a certain definite area per unit mass of liquid is attained. Rayleigh used this method and determined the surface tension of the film by the force necessary to pull a round plate from the surface.

He found that the minimum thickness of a film of castor oil which affects the surface tension of water is 13×10^8 cm., and from this reached the following conclusion (1899): "We conclude that the first drop in tension corresponds to a film one molecule thick." His results obtained with a film of ricinoleic acid, are represented in Fig. 16, and Table IX.

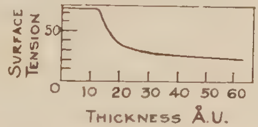

FIG. 16.—Surface tension (γ) of water plus a surface film of castor oil. The compression ($73-\gamma$) given by the figure inverted is more commonly plotted than the surface tension.

The force of compression is the difference between the surface tension of the film and that of pure water, and represents the force which must be exerted upon a float between the two in order to keep it at rest. Above a thickness of 80×10^{-8} cm. the surface tension is constant, that is, this is what is defined as a "saturated film." Rayleigh believed that at C, or a thickness of 50×10^{-8} cm., the film has increased to 2 molecules in thickness, but Devaux, who studied such films more extensively, considered that the lowering of the surface tension (increase of compressional force) is due to the closer packing of the molecules in the monomolecular film, which is the view held at present.

Langmuir[15] used the method of Pockels and Rayleigh to determine the relations for a considerable number of pure acids and alcohols. However,

TABLE IX

Typical Experiment by Rayleigh (1899) Upon Monomolecular Films

Thickness of Film × 10^8	Surface Tension	Force of Compression
00.0	73.0	0.0
12.8	73.0	0.0
14.1	72.5	0.5
15.3	71.6	1.4
15.9	70.7	2.3
17.0	68.6	4.4
17.8	66.4	6.6
18.4	62.0	11.0
19.3	57.5	15.5
20.8	52.6	20.4
22.9	44.2	28.8
26.7	35.4	37.6
30.4	31.0	42.0
45.8	26.6	46.4
63.7	24.4	48.6
81.7	23.0	50.0

instead of measuring the surface tension by their method, he determined the force upon a horizontal float between the film and the surface of the water. The most interesting feature of his results is that exhibited if it is assumed that the film is monomolecular. The area per molecule in a film of palmitic acid was found to be 21 Ångstrom units of area (1 *Å. U.*$^2 = 10^{-16}$ cm.^{2}). With cerotic acid, which has 26 instead of 16 carbon atoms, this area is only increased slightly to 25 *Å. U.*,^{2} while for myricyl alcohol, with 30 carbon atoms, it is 27. The area for tristearin, with three hydrocarbon chains of 19 carbon atoms each, is 66, or practically three times that for the corresponding acid. These facts are very simple evidence for the orientation of such molecules in films on water, but they give absolutely no indication as to whether the polar group is turned toward or away from the water.

Langmuir's method of measurement has been adopted and somewhat improved by N. K. Adam,[26] who has obtained a large number of results by its use. Harkins and Morgan[57] have also used the method for measurements upon derivatives of benzol, and for the investigation of films more than one molecule thick.

Fig. 17 represents Adam's work on palmitic acid at room temperature. The water used for the experiment is put into a shallow rectangular trough, made of brass 1 cm. thick, about 20 cm. wide, 60 cm. long, and 3 cm. deep. The edges are made plain in a milling machine. The trough is paraffined, which makes it possible to raise the water surface several millimeters above the edges of the trough. This surface is first swept clean by the use of glass strips, about 30 cm. long, which are paraffined. After this sweeping, a paraffined metal float, suspended from the beam of a balance is put across the water surface near one end of the trough, and a glass strip across the other end. A known mass of the palmitic acid or other substance to be used in the experiment, is put on the surface between this strip and the float. It is usually applied in the form of a dilute solution in benzol. The benzol aids in the spreading and evaporates rapidly. To prevent the film from passing around the ends of the float a minute jet of air is directed upon the surface at each end. This is delivered from a glass tip.

If the amount of palmitic acid applied is not too large, it is found that the float is not moved by the film. The next procedure is to move the glass strip closer and closer to the float, thus compressing the film. For a considerable distance the force exerted is usually too small to be detected by the balance. In experiment I, Fig. 17, the balance showed no effect until the area per molecule had been reduced to a little over 22 Ångstrom units. Then it was necessary to add weights to the balance in order to keep the float in place. Above 5 dynes per cm. compression the area decreases as a linear function of the compression until the point *H* is reached. Here the compression rises no longer, but the film "buckles" or crumples. Visible ridges appear, running as curved lines from one side of the trough to the other. The water on which this experiment was carried out had a small amount of impurity on its surface.

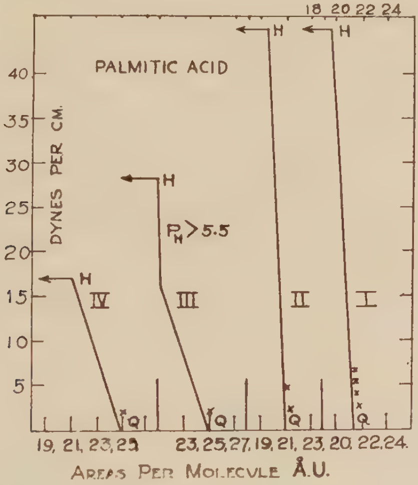

FIG. 17.—Areas per molecule of palmitic acid in its monomolecular films on water. At *Q* a force of compression is first noticed as the area per molecule is decreased, that is as the film is compressed. The film collapses at *H* at a compressive force which depends upon the experiment. The effect varies with the hydrogen ion concentration in the water and other factors.

When allowance is made for this "residual contamination," curve *II* is given. Extrapolation to the axis of area gives 21 Ångstrom units as the area of the non-compressed condensed film. Actually the compression begins to rise at an area of about 22, since at low compressions it is slightly "expanded." Such expanded films will be considered later. The lines marked *III* represent an experiment in which the water was acidified above p_H 5.5. The upper straight line is practically at the same position and of the same slope as on neutral water, but the lower line has a much smaller slope. Usually the film becomes solid at *Q*, but on acidified water the solidification delays until the steep portion is reached.

The experiments of Harkins and Morgan on the spreading of thin films on water and on salt solutions, are represented by Fig. 18a, b, c. The middle section represents experiments with stearic acid, which at zero compression gives an area per molecule of 19.2 *Å. U.* on water. It is of interest that one of the two experiments with water (Nos. 2 and 3) gave a lower straight line of small slope, which is totally absent in the other, although the two experiments were carried out under apparently identical conditions. The lower section cuts the axis at 21.1 *Å. U.* This value has been supposed to give the cross section of the head of the molecule, that is, of the carboxyl group. In most of the work this lower section did not appear with stearic or palmitic acid.

On a concentrated sodium chloride solution (mol fraction X of NaCl = 0.09) this area is 18.7 and the film is less compressible than on water. On calcium chloride (X = 0.1) the area is 21.2 and the film is much more compressible than on water. On potassium chloride solution the area is 21.9 and the film has nearly the same compressibility as on water. For palmitic acid on water the area is 20.2, or slightly higher than with stearic acid, but the compressibilities are nearly the same. Lauric acid, with 12 carbon atoms gives a much more compressible film, but it may be noted that nevertheless the relation of area to force of compression is linear. Lauric acid is too soluble to permit of the experiments being made upon pure water, so the water was made 0.1 M. with hydrochloric acid to repress the ionization of the lauric acid, and this solution was saturated with sodium chloride to lower the solubility still more. The line cuts the axis at 47.5 Å. U., which is plainly much too

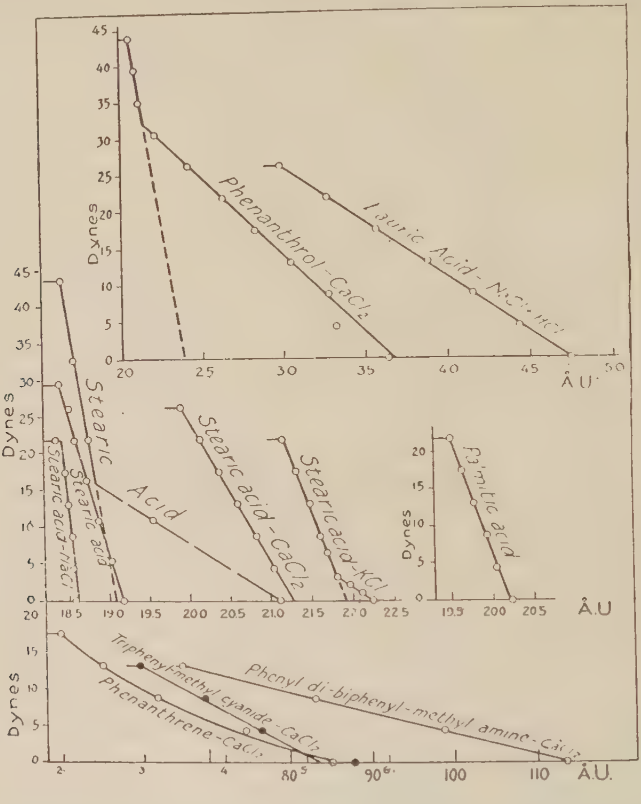

Fig. 18a.—Average areas per molecule in polymolecular films of phenanthrene and triphenyl methyl cyanide, and in monomolecular films of phenanthrol, lauric acid, palmitic acid, and stearic acid, on water and on salt solutions.

large to represent the area of the cross section of either the hydrocarbon chains or the carboxyl groups.

Experiments with derivatives of benzol exhibit relations of considerable interest. Thus, phenanthrol, with 3 benzol rings, gives an extrapolated area of only 23.8 Å. U., which is not far from 23.3, the cross section given for a single benzol ring by X-ray measurements (the mean thickness of the organic part of this film is 13.6 Å. U.). The more compressible phenanthrol film exhibits an initial area of 36.5 (thickness 8.0 Å. U.), that is, in the more loosely packed form the molecules exhibit quite a different type of packing. Phenanthrene has exactly the same molecule with the exception of the single oxygen atom of the hydroxyl group. This compound does not spread to a uniform film on water, but the addition of calcium chloride increases the spreading coefficient, S (see section 15), and a thick film is formed. At zero compression the area per molecule is very small and equal to 5.5 Å. U., so the film is remarkably thick, since the mean thickness is 53.3 Å. U. (of length). If this is the case the molecules of phenanthrene must lie in a film at least five molecules thick. There is no polar group in phenanthrene other than the so-called double bonds between the carbon atoms, and these are only slightly polar. The difference between this and the other compounds is exhibited by

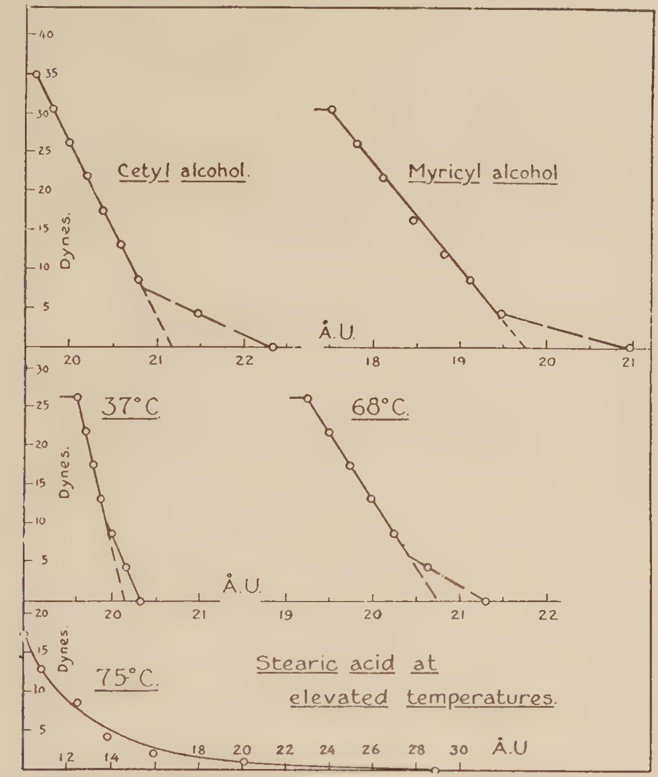

Fig. 18b.—Areas per molecule for films of cetyl alcohol, myricyl alcohol, and stearic acid on water.

the fact that the curve of compression shows a considerable departure from the linear relation, the force of compression increasing more rapidly than the area decreases. At 17.5 dynes compression, a thickness of 148 Å. U., and an area of 2 Å. U. the film collapses. Thus at collapse the film must be at least 14 molecules thick.

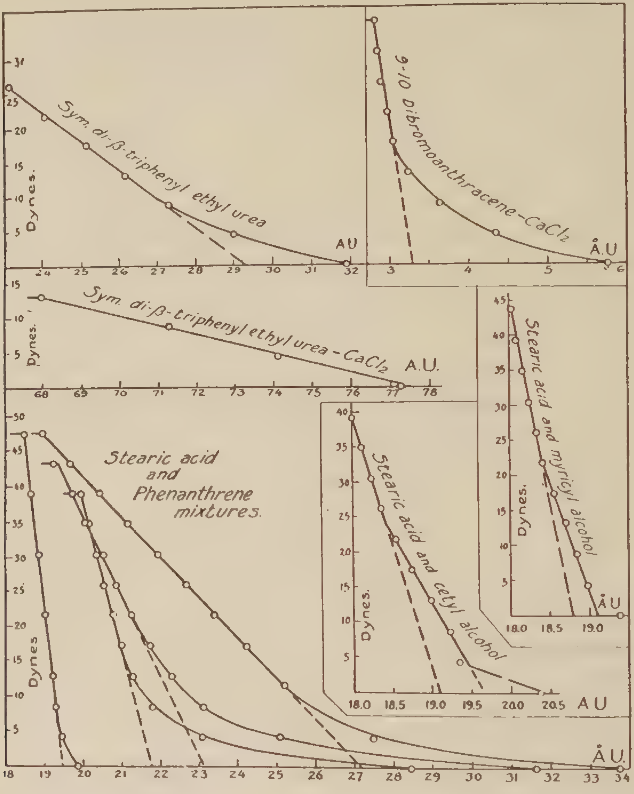

Fig. 18c.—Areas per molecule for a polymolecular film of dibromoanthracene and of di-β triphenyl ethyl urea on water, on a calcium chloride solution, for a monomolecular film of di-β triphenyl ethyl urea on a calcium chloride solution. Areas per molecule in the film for mixtures of stearic acid and myricyl alcohol, and of stearic acid and cetyl alcohol in equimolecular proportions. Area per molecule of stearic acid in mixtures of stearic acid and phenanthrene. The number of molecules of phenanthrene per molecule of stearic acid are for the four curves, proceeding from left to right: 0.4, 3.7, 6.4, 16.4. Evidently the phenanthrene forms a polymolecular film piled above a monomolecular film of stearic acid. The films become weaker as the relative content of phenanthrene increases, but the condensed films exhibit a linear relation between area per molecule (or per molecule of both kinds) of acid and compressive force.

It is of interest that with phenyl di-biphenylene methyl amine[*] at zero compression, the thickness of the film is 6 Å. U. The molecule contains 5 phenyl groups, and one polar amino group, which may be expected to bury itself in the water, but the extreme *thinness* of the film gives a strong suggestion that here too a part of the very large molecule (area = 113 Å. U.) may be flat on the surface (or that the molecule may be vertical and surrounded by water molecules). The film buckles at a very low compression, a little more than 13 dynes, and it is also the most easily compressible of all of the films investigated. Although the number of atoms in the molecule ($C_{31}H_{25}N$) is very considerable, the buckling occurs while the film is still very thin (11 Å. U.). However, with even a vertical orientation the greatest number of carbon atoms, one above the other, is nine, which would probably give a film of about this thickness.

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[*] This very large molecule gives a film in which the mean thickness of the organic part (excluding water) is the thinnest ever found for a film which obeys Hooke's law, and therefore possesses the characteristics of a condensed film.

Triphenyl methyl cyanide gives an area of 5.15 Å. U. at zero compression, or a mean thickness of 83 Å. U. for the organic part of the film, and collapses at a thickness of 139 Å. U. and a compression of 13 dynes per cm., or the same as that for the compound discussed in the previous paragraph.

The most interesting feature of the work of Morgan and the writer, as described above, is that it gives data on the compressive forces for both the thinnest (6 and 8 Å. U. thick), and also the thickest films ever measured.

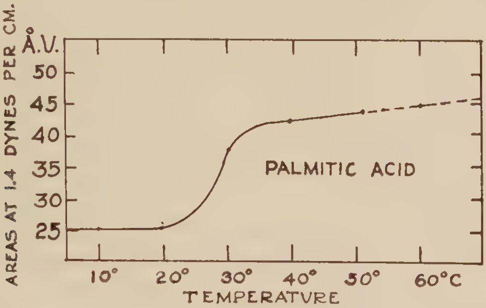

Fig. 19.—Effect of temperature upon the molecular area in a palmitic acid film on water under a low compressive force (1.4 dynes per cm.).

These thick films are respectively 53 and 83 Å. U. thick at zero compression, and 148 and 139 Å. U. at the point of buckling. One of these thick films, that of triphenylmethyl cyanide, acts like a monomolecular film in the sense that the relation between force of compression and area is linear. *That is, the film obeys Hookes' law, and therefore acts toward lateral compression as a perfectly elastic sheet.* In the case of the film of phenanthrene, however, the force increases more and more rapidly as the area decreases. That is, it appears as if the film is thickening uniformly by molecules sliding up over the others. At *H* the film buckles. That is, it no longer thickens all over, but only in certain portions, so the force of compression remains constant.

Fig. 19 plots the results of Adam upon the effect of a rise of temperature from 10° to 50° upon the area of a palmitic acid film at low compression (1.4 dynes per cm.). Between 10° and 20° the area is almost exactly constant, but above 20° it rises rapidly. The film evaporates in two dimensions, that is, the condensed film, which corresponds to a solid or liquid, evaporates into a film which acts as a gas in two dimensions. That is, the molecules in the film are no longer constantly in contact, but move at high speed, without, however, leaving the surface. This phenomenon was discovered by Labrouste[27] and explained by Marcelin.[28] The variation of the area of such films with the compression is shown in Fig. 20. It may be noted that these expanded or gaseous films exhibit at high temperature and dilution an expansion curve which suggests some of the isothermals given by an imperfect gas. None of the expanded films exhibit the linear relation previously discussed.

Fig. 20 plots data on the surface tension of aqueous solutions of the fatty acids of from one to ten carbon atoms per molecule. The values are those of Harkins, King, and Clark,[29] but Traube,[30] Drucker,[31] Whatmough,[32] Szyszkowski,[33] and others have made similar determinations, though they have not covered quite the entire range in length of the molecules. A knowledge of the slope of these curves together with the temperature gives the number of molecules per unit area by the use of the adsorption isotherm of Gibbs.[4] If Fig. 20 is inverted from top to bottom and also turned from left to right, then the line now marked 72.8 may be considered as the X-axis, and the curves become those of force of compression for films of these acids, but the abscissæ give the logarithm of the concentration of the solution instead of the area per molecule. With acetic and butyric acids the compressive force rises to as much as 45 dynes per cm. Tables X and XI collect the data for a number of various substances. Values given at 25 dynes compression are obtained by surface tension measurements upon the solutions. Langmuir[15] shows that triolein and trielaidin, each with three chains in the molecule, occupy extremely large areas of about 123 Å. U. per molecule.

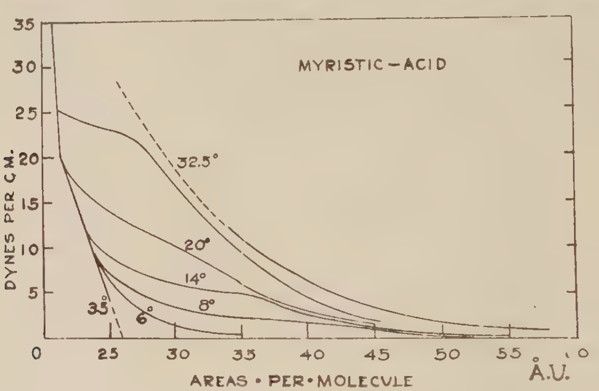

Fig. 20.—Expanded films of myristic acid at temperatures from 3.5° to 32.5°.

TABLE X

Areas in Å. U. per Molecule in Films of Various Organic Substances (at About 25 Dynes per Cm. Compression)

No. C Atoms	Normal Acids	Alcohol	Iso-alcohol
1	(57) H	——	——
2	(50) H	32 T.L.	——
3	39 H	29 T.L.	34.7 T.L.
4	36 H	——	27.8 T.L.
5	32 D	——	27.8 T.L.
6	31 D	——	——
7	34 H	——	——
8	——	——	——
9	32 H	——	——
10	31 H	——	——

Areas below calculated to zero compression where marked A or H and M

16	21 L	——	——
	20 A	——	——
	20.3 H and M	——	——
18	22 L	——	——
	19.6 H and M	——	——
26	25 L	——	——
Triolein			126 L
Trielaidin			120 L

L—Langmuir.
A—Adam.
H—Harkins, King and Clark.
H and M—Harkins and Morgan.
T.L.—Traube calculated by Langmuir.
D—Drucker calculated by King.

TABLE XI

AREAS PER MOLECULE OCCUPIED ON A SURFACE BY BENZENE DERIVATIVES

EXPERIMENTS BY HARKINS AND GRAFTON

(at about 25 dynes per cm. compression)

	Areas in A.U.
Phenol	36.6
Pyrocatechol (ortho)	55.0
Resorcinol (meta)	96.0
Hydroquinol (para)	(185.0)
Pyrogallol	42.7

FILMS ARRANGED IN ORDER OF INCREASING THICKNESS AT COLLAPSE

EXPERIMENTS BY HARKINS AND MORGAN

(Monomolecular Films above and Polymolecular below. Dimensions in Ångstrom units. $CaCl_2$ represents an aqueous solution of the salt.)

Substance of Film	On	At Zero Force		At Collapse	
		Area	Thickness	Area	Thickness
Phenyl dibiphenyl methyl amine	$CaCl_2$	112.0	6.0	80.0	8.4
Phenanthrol	$CaCl_2$	36.5	7.0	21.3	12.0
Stearic acid	H_2O	19.3	28.5	18.4	30.0
Symmetrical di-β-triphenyl ethyl urea	$CaCl_2$	77.5	12.2	68.0	14.0
(polymolecular on water)	H_2O	28.3	33.4	22.6	42.0
POLYMOLECULAR FILMS					
9,10-Dibromo-anthracene	$CaCl_2$	5.9	47.0	2.5	111.0
Triphenyl methyl cyanide	$CaCl_2$	5.2	70.0	5.0	120.0
Phenanthrene	$CaCl_2$	5.6	47.0	2.0	132.0
Di-β-naphthylamine	H_2O	2.7	125.6	2.15	158.0
Hexachlorobenzene	$CaCl_2$	5.2	45.0	0.95	248.0
α-Bromonaphthalene	$CaCl_2$	1.5	187.0	0.6	405.0

Monomolecular Films of Water on Salt Solutions.[54]

A salt is much more polar than water, so salt is negatively adsorbed from the surface of the aqueous solution; that is, water is positively adsorbed on the surface of a salt solution. The extent of the adsorption of the salt is calculated most conveniently by the use of the writer's modification [54] of the equation of Gibbs: For di-ionic salts

$$\mu = \frac{\alpha c}{2RT}\left[\frac{\partial \gamma}{\partial(\alpha c)}\right]_{T, A}.$$

and for any salt

$$\mu = \frac{\alpha c \pm}{\nu RT}\left[\frac{\partial\gamma}{\partial(\alpha c \pm)}\right]_{T,A}.$$

The concentration in mols of salt per 1000 g. of water is given by c, and the activity coefficient of the salt by α.

If it is assumed that the density of the water in the surface film is the same as that of water in bulk, and if the concentration of the solution is supposed to remain constant until at a distance t, from the surface, it falls to zero, then this mean thickness, t, of the water film is given by the equation

$$t = -\frac{1000\,\alpha}{\nu RT}\left[\frac{\partial\gamma}{\partial(\alpha c_{+})}\right]_{T,A_0}$$

The thickness of the water film on various salt solutions is given below.

Mols of Salt per 1000 Grams Water	Thickness of the Water Film on Salt Solutions in Ångstrom Units Lithium Chloride	 Sodium Chloride	 Calcium Chloride
0.1	3.5–4.0	3.5–4.0	4.4
0.5	3.3	3.4	4.0
1.0	2.4	3.2	3.8
3.0	2.0	2.6	2.6
4.0	—	2.35	—
5.0	—	2.30	—

The cube root of the volume occupied by a molecule of water in liquid water at 20° is 3.1 Ångstrom units, so the films of water on the above salt solutions are evidently monomolecular. The values were obtained by H. M. McLaughlin, E. C. Gilbert, R. W. Wampler, and the writer.[54] In dilute solutions the water film apparently has the same thickness on solutions of lithium and sodium chlorides. In more concentrated solutions the thickness is smaller on lithium chloride solutions, but only because the activity of lithium chloride is much greater. At least in dilute solutions the water film is thickest on calcium chloride solutions. The thickness of the water film decreases with the activity (effective concentration) and increases somewhat with an increase of charge on the ions provided the activity is not too different.

18. THE INFLUENCE OF THIN SURFACE FILMS UPON THE EVAPORATION OF WATER

Recent work by Hedestrand[48] indicates that a monomolecular film of oleic or palmitic acid upon water does not diminish the rate at which the water evaporates into a current of air moving over it. Harkins and Morgan had obtained a result in perfect agreement with this, by allowing the evaporation to take place into still air. The water vapor was condensed by a metal surface at — 20° C., at a distance of 1 cm. This latter method allowed the compression to be varied by a movable barrier. These results indicate the monomolecular films contain water as well as the organic substance, and furthermore that the film is in anything but a static condition. Our results indicate that films several molecules thick (5 to 10) lower the rate of evaporation slightly. If these experiments had been carried out in a vacuum a considerable lowering of the rate of evaporation would have been found as produced by the monomolecular film. Such experiments are difficult, but the writer has devised a method for the work, and expects to investigate the problem as soon as the small amount of time necessary is available. When air is present over the surface nearly every molecule which succeeds in jumping out of the surface jumps back in again, but this is not true when the evaporation into a vacuum takes place. Thus isotopes, such as those of mercury, are readily separated by vaporization into a vacuum, but they are not separated at all to an appreciable amount by evaporation into air at ordinary pressures.

Layers of Palmitic and Stearic Acids upon Glass.

Recent X-ray investigations of thick films of fatty acids upon a glass surface show that the molecules arrange themselves in layers one molecule thick parallel to the surface of the glass.

19. Surface Tension and Hydrogen Ion Concentration

An active muscle is slightly acid in reaction, and a muscle at rest slightly alkaline. This suggests that it may be of some importance to physiology to determine the effect of a change of hydrogen ion concentration upon surface and interfacial tension. The tension at the interface between "mustard gas" (β-β-dichloroethyl sulfide) and water is 28.36 dynes per cm.[34] at 20°. If the water is 0.1 molar with respect to hydrochloric acid, this is raised slightly to 28.90, but if of the same concentration with respect to sodium hydroxide, it is reduced very greatly, to 12.78, or 44 per cent of the original value. Bases have similar effects when present in the aqueous phase of a number of other two component systems with two liquid phases. The interfacial tension between water and ethyl oleate is 21.34. If the aqueous phase is made 0.1 molar with sodium hydroxide, this falls to the extremely low value 0.3 dyne per cm. A plot of the interfacial tension against the log, of the OH^- ion concentration has the form of a typical adsorption curve for a capillary active substance.

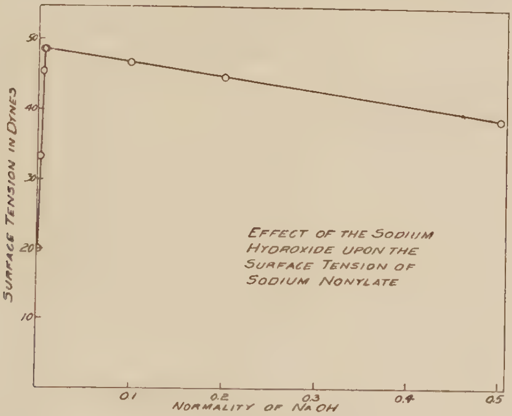

FIG. 21a.—Effect of the addition of sodium hydroxide upon the surface tension of a tenth molar solution of sodium nonylate in water.

The effects of acids and bases are most pronounced when a capillary active substance is dissolved in the aqueous phase. Thus the surface tension of water is 72.80 dynes per cm. at 20° and this is reduced to 20.0 as the aqueous phase is made 0.1 molar with respect to sodium nonylate.[35] If sodium hydroxide is added the surface tension rises rapidly to 33.4 at 0.001 M. and to 48.8 at 0.008 M., the concentrations being those of the base. Further additions decrease the tension as a linear function of the concentration (Fig. 21a).

The most varied and interesting effects due to a change in the hydrogen ion concentration are produced in systems in which soaps are present as solutes (Fig. 21b). Such systems will be considered in connection with the discussion of emulsions. The most interesting result obtained is that with oleic acid in benzol (0.1 M.), and sodium hydroxide and sodium chloride of the same concentration in water, the interfacial tension between the two phases drops to about one thousandth of the value for water against benzol (35.0), or to 0.04 dynes, the smallest interfacial tension ever determined for immiscible phases. Although the two phases are immiscible in the molecular sense, they emulsify readily.

The interesting feature of this work [60] is that the chemical energy of union between oleic acid and sodium hydroxide seems to aid directly in building up the interface, and takes the place of a part of the free interfacial energy.

TABLE XII

Effects of Salts upon the Interfacial Tension between Water and Oil with a Film of Sodium Oleate Produced by Chemical Action

Base or Salt Added to Aqueous Phase			Surface Tension in Dynes/Sq. Cm.	
NaOH, *N*	NaCl, *N*	$CaCl_2$, *N*	Olive Oil	Paraffin Oil
—	—	—	—	40.6
—	—	—	+0.001 N.	Oleic acid in oil
—	—	—	24.11	31.05
0.001	—	—	7.3	7.2
0.001	0.15	—	0.002	—
0.001	—	0.0015	9.88	9.65
0.001	0.15	0.0015	6.88	7.48
0.001	0.30	0.0030	6.36	7.12
0.001	0.45	0.45	6.70	7.36
0.001	0.60	0.0060	7.31	8.20

20. Crystal Form and Surface Energy

According to Wherry,[36] angle distortion in crystals, or the development of vincinal faces, is often due to the surface or interfacial tension, which tends to make a mass of material spherical. "In the case of liquid drops it succeeds; but in crystals it cannot go so far." In the mineral fluorite, for example, the cube is often replaced by a vincinal tetrahexahedron. Since surface tension is ever present, the development of such vincinal faces is to be looked upon as a normal phenomenon of crystals, and the slopes of these faces as being not chance matters, but definite expressions of forces inherent in and characteristic of each substance." Also the etch figures produced upon the surface of a crystal by the application of minute amounts of solvents are often largely affected by the interfacial energy.

21. The Determination of Surface and Interfacial Tensions

Although the determination of the surface tension is fundamentally a simple problem, the history of the methods employed for this purpose may be best described as a comedy of errors. The errors were of two types: (1) in the experimental methods, and (2) either in the fundamental theory or in the theory of the corrections involved. In general if one of these forms of error was avoided the other was embraced, so that even in practically all of the best work errors of 3 per cent were made, and in the poorer work the error rose to 15 or 20 per cent or even more, and was often especially high in the determination of interfacial tension.

The best general method for use in connection with work on the problems of colloids or of physiology, or those of industrial chemistry at ordinary temperatures, is the determination by means of the drop weight. It gives better results than any other method when used with cheap apparatus and only ordinary care. Thus students by the use of an apparatus which costs only two dollars quite commonly obtain a value for the surface tension of water during their first half day of work, which is within 0.3 per cent of the best value now known. Obviously this is done only by careful and well directed work. The criticisms to which this method has been subjected are due to the fact that it is often used with entire disregard of its fundamental principles, and without the application of certain absolutely essential steps in the calculation of the results from the data. Errors are also due to the use of the stalagmometers and dropping pipettes sold by apparatus houses; instruments which have been constructed with entire disregard of most of the conditions essential for accurate work.

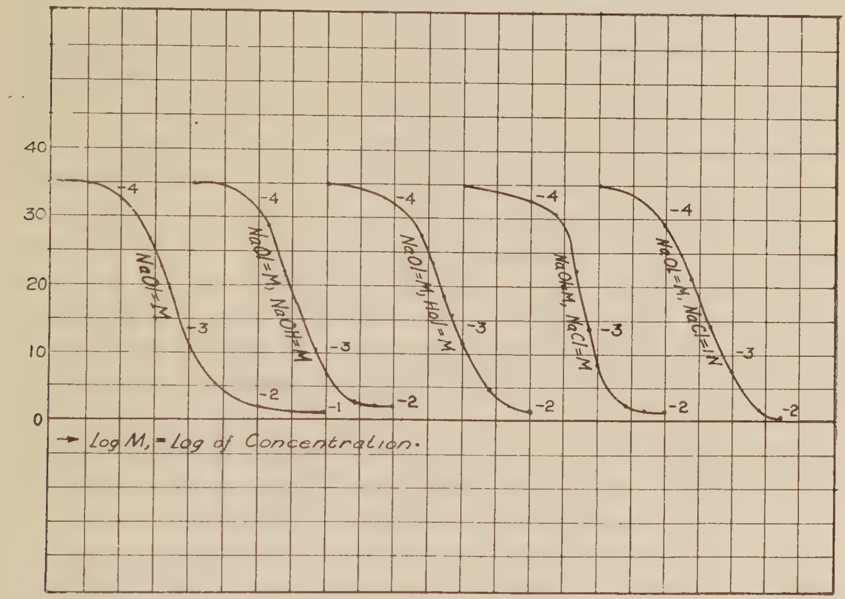

FIG. 21b.—Effect of the addition of sodium hydroxide and other substances on the interfacial tension between benzene and aqueous solutions of a soap.

The drop weight method has been converted into a method of high precision by Harkins and Brown,[37] who have established extremely simple methods of calculation which enable the worker to obtain by its use the results which would be given by the capillary height method when used under the best conditions.

The capillary height method involves on the whole much more careful manipulation and measurement for the same precision of results, and is not so well suited for general work on interfaces. It has, however, the advantage that its theory is the simplest of all known methods. This method has been studied critically and given high precision by Richards, Coombs, and Speyers [38] and Carver at Harvard University, and by Harkins and Brown [37] and by Young, Gross and Harkins at the University of Chicago.

The determination of the maximum pressure in a bubble has also the advantage of a simple theory, though not so simple as that of the capillary height. It has recently been given a considerable degree of precision by the work of Sugden,[39] though it has not as yet attained quite the high accuracy of the two preceding methods for work at ordinary temperatures. It has the great disadvantage that it is not applicable to the measurement of interfacial tension, nor is it capable of measuring the surface tension of a liquid against its own vapor without the presence of a gas.

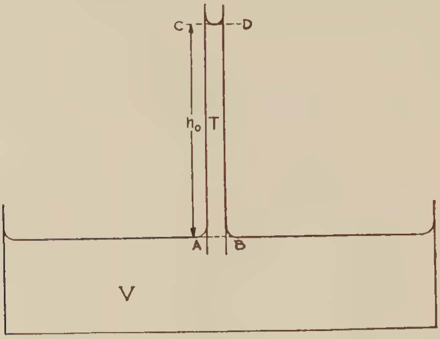

FIG. 22.—Diagram illustrating the determination of surface tension by the capillary height method.

22. THE CAPILLARY HEIGHT METHOD

As an absolute method the determination of surface tension by a measurement of capillary height depends upon very simple relations made evident by Fig. 22. A narrow tube (T) of known constant; internal diameter dips into the liquid in a vessel or tube (V) so wide that the large meniscus is not raised appreciably by capillarity. Then there will be hydrostatic equilibrium between the liquid in V and the part of T below the dotted line AB of the figure.

Provided the gas and vapor around the tube is of negligible density the whole weight of the liquid in T above this line must be held up by the surface tension of the upper meniscus. Suppose that the liquid wets the wall of the glass tube and that the angle of contact between the liquid and the glass is zero. Under these circumstances there will be a vertical film of water on the glass which exerts a pull along a length equal to the circumference of the tube or to $2\pi r$. The pull of a film of this length is $f = 2\pi r\gamma$ and this tension supports the liquid in T.

The weight of this liquid up to the line CD at the bottom of the meniscus is $W = \pi r^2 h_0 d$ where d is the density of the liquid. The total weight supported by the surface tension of the liquid is this weight plus that of the upper part of the meniscus (W'). Thus the force upward is

$$f_u = 2\pi r\gamma \tag{1}$$

and that downward

$$f_d = \pi r^2 h_0 g d + W' \tag{2}$$

At equilibrium therefore: $f_u = f_d$ or

$$\gamma = \tfrac{1}{2} r h_0 g d + \frac{W'}{2\pi r} = \tfrac{1}{2} r h_0 g d + \frac{mg}{2\pi r}. \tag{3}$$

If the capillary tube has an extremely small internal diameter then W' is negligible and

$$\gamma = \tfrac{1}{2} r h_0 g d$$

If the vapor around the tube T has an appreciable density d', then a part of the weight of the liquid is balanced hydrostatically by the vapor, and equation (2) becomes

$$f_d = 2\pi r^2 h_0 g(d - d') + gv(d - d')$$

in which v is the volume of the meniscus (*i.e.*, of the liquid above the line CD).

Equation 3 is changed by this density correction to

$$\gamma = \tfrac{1}{2} r h_0 g(d - d') + \frac{gv(d - d')}{2\pi r} \tag{3¹}$$

It is simpler to include the second term of the right hand side in the first term by making a correction to the height h_0 such as will give the volume of the meniscus when multiplied by πr^2. Thus Poisson showed that for very narrow tubes the volume of the liquid of the meniscus is such that it would give a cylinder of liquid of the diameter of the tube and with a height nearly equal to $\frac{r}{3}$, thus the height h to be used in calculating the surface tension is:

$$h = h_0 + \frac{r}{3} - 0.1288\frac{r^2}{h}$$

Rayleigh found that for somewhat wider tubes

$$h = h_0 + \frac{r}{3} - 0.1288\frac{r^2}{h} + 0.1312\frac{r^3}{h^2} \tag{4}$$

The surface tension is, therefore

$$\gamma = \tfrac{1}{2} r h g(d - d') \tag{5}$$

In using the capillary tube method for absolute determinations it is essential to observe certain precautions:

(1) The outer tube should have a large diameter, that is, the lower meniscus should be about 8 cm. or more in diameter and the small capillary should not stand at its center, but should be used as a side arm, or be placed very near one edge of the large meniscus.

(2) The capillary should be tested carefully for uniformity by the use of beads of mercury of various lengths. The diameter may be calculated from the difference in weight and length of two beads of mercury, one at least twice as long as the other. The centers of both of these beads should lie as nearly as possible at the position to be used for the meniscus of the liquid during a measurement of its surface tension.

This measurement serves to give the mean diameter of the tube. It has been found by Young and Gross that the diameter of a capillary tube selected with great care showed a variation of diameter represented somewhat nearly by a sine wave of a wave length of 9 centimeters. In order to determine the diameter of the tube at any point used for a measurement, it is therefore essential to determine the variation from the mean at each point by the determination of the change in length of a much shorter bead of mercury, as it is moved along the tube.

(3) The capillary should be as nearly circular in cross section as is possible, and a correction should be made for its ellipticity.

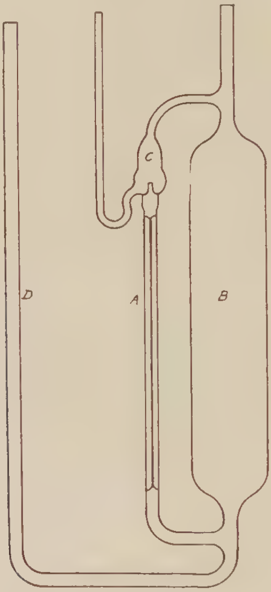

Fig. 23.—Apparatus for the exact determination of surface tension by the capillary height method.

(4) Great care should be observed in the lighting of and focusing on the large meniscus.

If this is properly done the position of the cathetometer telescope will exactly coincide with that obtained by sighting upon a fine point which has been lowered exactly to the surface of the liquid by a slow motion screw. Such a point may be set to any required degree of precision. At the moment of contact with a clean point a disturbance of the surface around the point is easily visible.

(5) The walls of the capillary should be wet with the liquid as thoroughly as possible. Steaming out the capillary with the vapor of the liquid is the best known method of insuring good wetting, and evacuating the capillary just before filling is helpful. Steaming also gives a high degree of cleanliness. The measurement should be taken just after the meniscus has *fallen* to a position of rest, since with a rising meniscus the contact angle is less apt to be zero.

The time necessary for the meniscus to fall to rest may be 30 minutes, or even more. With an extremely clean capillary and meniscus the same reading should be obtained on a meniscus which has risen to rest as with one that has fallen to rest, and the reading often remains constant for days. To obtain a clean meniscus the water in the capillary tube should be run up over the top of the capillary tube, and this top should be protected by a trap for the water which overflows. By the use of the trap the requisite cleanliness may be obtained without steaming.

(6) The difference between the level of the liquid in the large tube or vessel and the meniscus in the capillary may be determined by the use of a high grade cathetometer preferably with two telescopes, which has been standardized by the use of a millimeter scale ruled on invar and tested by the Bureau of Standards or some similar bureau.

If the level of the large meniscus is determined by focusing the telescope of a cathetometer upon it, great care should be taken to focus upon the center of the meniscus, and this center should be at least 4 cm. from all points at which the meniscus is touched by any object.

The apparatus used for the absolute determination of the surface tension of liquids held two capillary tubes each of uniform bore. Uniformity is of extreme importance, but it may be mentioned that this one item in the work took the time of two investigators for two months to obtain the two tubes. These are set into the apparatus by gold collars above and below in such a way that when the level on the apparatus is leveled, the tubes are vertical. The glass on the front of the apparatus is optically plane. The differences in level are obtained by the use of an accurate cathetometer. Fig. 23 shows the capillary height apparatus used by Richards, but with a trap just above the capillary. This trap, added by Young and Gross aids greatly in securing a pure surface at the meniscus.

23. Capillary Height Method at an Interface

Interfacial tensions are of extreme importance in connection with colloids. The principles involved in making the determinations by the capillary height method are no different than those in the preceding section as applied to surface tension. The whole difference from the experimental standpoint is that the upper liquid must have its upper surface above the upper opening in the capillary tube. The method is more delicate than at a surface, since the capillary height for a given diameter of capillary may be five to twenty times greater. This makes it essential to observe the first precaution listed below:

1. The diameter of the lower meniscus needs to be even greater for use with interfacial than for surface tensions.
2. In interfacial work the angle of contact is not known to be always zero.
3. The densities of the liquids must be determined with considerable accuracy, since it is the difference of density, $d - d'$, which is used in calculating the tension. While this factor is also used for surface tension determinations, d' is very small except at high corresponding temperatures, where the preceding sentence applies.
4. Each of the two liquids is soluble in the other in general, and if equilibrium is not attained the density difference is not the same as for equilibrium. In some cases the interfacial tension may be affected by the non-equilibrium condition.
5. The shaking or stirring used to produce equilibrium commonly produces a dilute or concentrated emulsion, which may affect the determination.

If a cathetometer is available a U tube, joined both above and below, may be used for the determination. One arm should be about 12 cm. in diameter, and the other of the order of 1 mm. Obviously there must be an opening for the admission of the two liquids, and commonly this is placed above the larger tube. Such an apparatus may be evacuated, and with a smaller capillary diameter is also available for work on surface tension, and has been used for this purpose by Richards and Coombs.

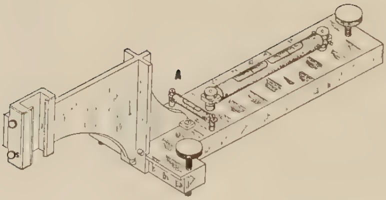

Fig. 24a.

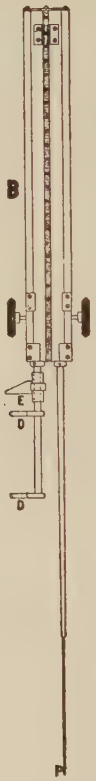

Fig. 24b.

Fig. 24a and b.—Stand, and holder with graduated scales, for supporting sharp point and capillary tube.

Harkins and Humphery[40] have designed an apparatus for work on interfacial tension without the use of a cathetometer, which gives results to the highest degree of accuracy.

Fig. 24a shows the base of the tube and scale holder, which make certain their vertical position. Fig. 24b shows the scale with two movable verniers, one for reading the height of the tube and one for reading the height of a sharp point of platinum. In Fig. 25, the large meniscus, which should have a diameter as great as 12 cm., is in C. The capillary is put at the extreme right of the tube *MH*, and the long platinum point is inserted in the tube *N*, which is exactly at the center of the top of the bulb *C*. It may be noted that to correspond with the position of the scale of Fig. 24b, the position of this tube should be the mirror image of that given. The capillary tube is held in a gold plated or platinum rod bored out at the bottom to exactly fit the upper part of the tube. The gold plated rod is held in the supports *DD* and against the stop *E*. Just above the top of the capillary the metal rod has openings larger than the inside bore of the capillary, which lead into the space just above its opening. The outside of the glass capillary carries a very fine graduation where the meniscus is to be observed. The two verniers are adjusted and read

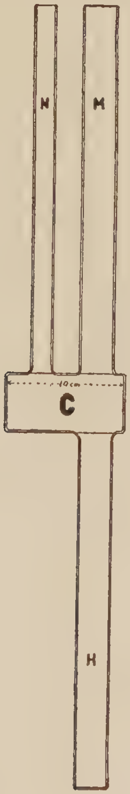

Fig. 25.—Vessel for holding two liquids whose interfacial tension is determined.

while this graduation is just level with the platinum point. The tube of Fig. 25 is then put in place, and the tube raised until the graduation comes exactly at the small meniscus. Then the platinum point is lowered until it just touches its bright mirror image in the large interface. The moment the two touch the interface gives a slight jump upward around the point, which should not be moved further. This adjustment is extremely exact, and the apparatus will determine the interfacial tension as accurately as is obtained by the best methods for surface tension.

There are, however, several errors which affect determinations of interfacial tension much more than surface tension, but these are independent of the apparatus.

23. The Angle of Contact between Liquids and Glass

One of the great advantages of the drop weight over the capillary height method for determining surface or interfacial tension lies in the fact that the former is entirely independent of what is known as the angle of contact between the liquid and glass, provided the tip is properly made and of a suitable diameter. The capillary height method is, on the other hand, dependent upon the angle of contact, since with any other than a zero angle equations (1) and (5) for the capillary height method become converted into

$$f_u = 2\pi r\gamma \cos\vartheta \quad (1') \qquad \gamma = \frac{1}{2}\frac{rhg(d - d')}{\cos\vartheta} \quad (5')\ *$$

and the term $\cos\vartheta$ must be included in the other similar equations.

In 1919 Harkins and Brown gave convincing, but indirect evidence that the angle of contact is zero for four liquids: water, benzene, carbon tetrachloride, and ethylene dibromide. It was found that the angle of contact is very small for these liquids, and that it is the same within the limits of error of highly precise measurements for all four. More direct evidence was given in an independent investigation by Richards and Carver,[38b] who proved by optical measurements that the angle of contact is zero for water, benzene, carbon tetrachloride, chloroform, and ether. Thus at the present time there is evidence that the capillary height method is applicable to six liquids: for the others the angle of contact is unknown, though it is probable that it is zero for most liquids. No test has been made of the angle of contact for any interface, but the work of this laboratory indicates that it is usually very small.

Since the drop weight method, itself independent of contact angle, has been standardized by the use of four liquids whose angle is zero, this method gives for any other liquid or interface between two liquids, the correct value: that is, it gives the value which would be given by the capillary height method with a zero contact angle.

24. Drop Weight Method for Surface Tension

The drop weight method has about the same degree of precision as that in which the capillary height is measured, but it is experimentally much more simple, and gives much more accurate data when only ordinary care is used. The method has been very much misused, and it is too much to expect any method to give good results when its most fundamental principles are violated by many workers in industrial or in physiological chemistry on account of ignorance or laziness.

The theory of this method has been considered by Rayleigh,[41] and particularly by Lohnstein.[42] Kohlrausch and Ollivier have also discussed the method. That it is now capable of giving accurate results is due to the work of the writer and his two associates, E. C. Humphery and F. E. Brown, who began their study in 1912.

The cross section of a drop weight apparatus is shown in Fig. 26.† For work of high precision the apparatus is supported by a heavy iron rod of 1 inch in diameter held upright by a heavy iron tripod which rests upon a concrete pier. During a determination the box is suspended in the water of a thermostat from its outside support. The most important part of the appa-

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* Note that h is not the actual, but is the *corrected* height.

† For further details see *J. A. C. S.*, 38, 247 (1916).

ratus is the tip *D*, Fig. 26. A straight heavy walled capillary tube of glass (Jena glass makes excellent tips) is clamped in a precision lathe, which causes the tip to rotate at a considerable speed in one direction. The tube is ground off along the side near the end by a wheel of fine carborundum which rotates at high speed in the same direction, which means that the surface of the glass and of the wheel are moving in opposite directions over the area of contact. Finally the surface of the glass is polished with rouge while rotating in the lathe. Such tips are accurately round. The next step is to grind off the tip of this cylinder until it is plane and at a right angle with the end. It is most important that the edge of the tip be kept entirely sharp, so that no flaws are observable under a microscope of low power (magnification of 10).* A cylinder of brass of about 5 cm. diameter and 2 cm. thickness is bored in the center so that the hole is vertical and just large enough to slip over the tip. This hole is finished on the lathe. The tip is sealed into this hole by a mixture of beeswax and rosin, or by Wood's metal, with the tip projecting very slightly. Then the tip and the cylinder are ground by carborundum in water upon a plane block of steel. In this way it is possible for the edges to be made perfectly sharp, while the bottom of the tip is still left rough. This roughness is of considerable advantage, since it aids in keeping the tip wet to its extreme edge. The diameter of the tip is measured by a microscope moved by a micrometer screw.

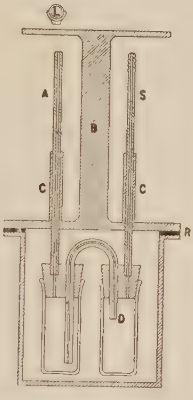

Fig. 26.—Cross section of drop weight apparatus of Harkins and Brown. The tip, weighing bottles, and windows are of glass, the rest of the apparatus, nickel-plated brass. The design is similar to the earlier glass apparatus of Morgan.

Control of the Drop.

After the liquid whose surface tension is to be determined has been added to a weighing bottle this is fastened to or put under that end of the capillary inverted U tube which has not been ground into a tip, an empty weighing bottle is pushed onto the stopper in which the tip is fastened. This is preferably of glass and the fit must be very tight. The greater part of the drop is pulled over by suction on the tube *S* (Fig. 26). Gravity alone is allowed to control the formation of the last tenth of the drop. To accomplish this, the level of the liquid in the supply bottle is made just a little higher than the level of the tip and by applying suction the drop is drawn over to as nearly full size as is possible without causing the drop to fall under the influence of the suction. How nearly the full size may be approached depends on the skill of the operator. Then the drop is allowed to complete its growth and fall under the influence of gravity. A second drop is allowed to form and fall under the influence of gravity alone. The time between the fall of the first drop and the fall of the second drop, when the whole drop is allowed to fall by gravity alone, is called the drop time. A supply cup 2 to 3 cm. in diameter was used, and the change in the rate of formation of drops during a 30-drop run, was very small. Frequently 3 successive runs were made from one filling of the supply cup, with correspondingly slower rates of formation for the drops of the later runs.

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* It is simpler to first grind the end of the tube, then cement on the end a glass disc to protect the edge, and grind off the side of the tube and disc together in the lathe. On melting the cement, the edge of the tip is found to be without flaws under a magnification of 40.

Speed of Formation of the Drop.

When the rate of formation is faster than a drop in 3 minutes, on ordinary sized tips, some of the liquid streaming from the tube seems to force its way into the falling drop during the time of detachment, and consequently, a drop formed rapidly is heavier than one formed slowly. The following series of runs was made by dropping water from a glass tip whose radius was 0.24456 cm.:

TABLE XIII

	Drop Time		Drop Weight in Grams
	Min.	Sec.	
	1	20	0.07191
	1	45	0.07187
	3	30	0.07179
	6	00	0.07172
	9	00	0.07174
	10	00	0.07175
	11	20	0.07173
Slower than	11	00	0.07172

The variation in the weights of the last 5 runs is probably due to experimental errors. The drop weight rises rapidly as the time of formation is reduced below that given in the above table. It will be seen that on a tip of this size three minutes is too short a time for the formation of the proper drop.

Collecting and Weighing the Drops.

In our experiments, before the apparatus was put in the thermostat, the level of the liquid in the supply cup was adjusted so that the drop time was about 5 minutes for small and medium sized drops, and up to 12 and 15 minutes for large drops. The time required for a 30-drop run, when the drop time was 15 minutes, would have been 7.5 hours, had we permitted gravity alone to form the drop. The possible errors due to evaporation would more than compensate for the accuracy gained by slow formation; so the drops were drawn to nearly full size and only the last fraction of each drop formed slowly. The average time required for an experienced operator to draw over and drop 30 drops is 30 minutes. Any form of suction apparatus, which is susceptible to quick and accurate control, can be used, but we found that suction with the mouth was satisfactory. A soda-lime tube was inserted in the rubber tube connecting the dropping cup and the mouth, as danger of contamination was apprehended.

Our method of making a run is: clean, mount and level a tip,[40] adjust the level of the liquid in the supply bottle, so that the drop time is about 5 minutes, force the liquid back through the capillary, so that no drop is on the tip, place a clean weighing bottle on the plug * around the dropping tip, adjust the protecting box of the apparatus in the thermostat. In our work, depending on the difference in temperature between the thermostat and the room, a period varying from 15 to 40 minutes was allowed for the liquid to reach the proper temperature. Then the first drop was drawn over, and, by suction or pressure, kept at full size for 5 minutes. The purpose of this was to saturate the space in the dropping cup with vapor, so that the first drop, as well as all others, would fall in its own saturated vapor. Thirty drops were drawn successively, to as nearly full size as the operator could judge, and then allowed to detach and fall under the influence of gravity. The residual drop was forced back into the supply cup, the apparatus removed from the thermostat, and finally, the weighing bottle was cooled with ice water for ½ minute, to prevent loss of vapor, and then removed from the plug and stoppered; another weighing bottle was put on the plug, the protecting box replaced, and the apparatus again immersed. As the apparatus was out of the thermostat 3 minutes or less, it would return to the desired temperature in a very short time. The bottle and drops were weighed while we were waiting for the apparatus to reach temperature equilibrium. This procedure was repeated for the second weighing bottle and the first weighing bottle was returned to the apparatus for the blank run. The blank run was made exactly like the others, except that the same length of time was taken for dropping 5 drops into the weighing bottle, as had been required to drop 30 drops into the same bottle in the ordinary run. After this run, the second bottle was returned to the apparatus and a blank run made in it. The weight of the bottle and 30 drops, diminished by the weight of the bottle and 5 drops, gives the weight of 25 drops. The distillation from the convex drop to the concave surface in the bottle, the weight of the vapor in the bottle, and all other causes for loss or gain in weight, are nearly the same in both cases, and are approximately eliminated. To prevent vaporization of the liquid in the weighing bottle the bottom may be covered with a non-volatile paraffin oil, but extreme care must be exercised to select an oil which is sufficiently non-volatile. This differs from Morgan's method [59] of determining the weight of a drop in only a few particulars.

The method described above is capable of giving reproducible results to a precision of 0.02 per cent when carried out under the most favorable conditions.

Principle of the Drop Weight Method.

If the drop which hangs at the end of a tip were cylindrical and of the same diameter as the tip, it is evident that the maximum weight of drop which could be supported is exactly equal to the weight of the liquid upheld in a capillary tube of the same diameter. This is because in both cases the force

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* This weighing bottle should be so ground to the plug as to give a very tight fit. Otherwise air is drawn through the crevice and this may evaporate some of the liquid which has dropped into the weighing bottle.

of surface tension acts on a line $2\pi r$ long, so the force is $2\pi r\gamma$. Lohnstein assumed this to be the force holding up the drop when the tip has an extremely minute diameter, that is

$$W = 2\pi r\gamma \tag{1}$$

and this weight has been defined by Harkins and Brown as the weight of an ideal drop.

Actually, however, the drop does not break away from the exact edge of the tip, but the liquid breaks apart some distance below the edge, leaving a "pendant" drop. Observation shows that with tips of moderate size the drop is constricted where the break occurs to a diameter less than that of the tip. Thus the drop which falls should have a weight smaller than corresponds to equation 1. As has been stated Lohnstein solved this problem mathematically, but only to an accuracy of 4 per cent in the region of ordinary determinations. Harkins and Brown have determined the values of the corrections involved by comparing the results of the drop weight method with those obtained by the capillary height method under the best conditions for the attainment of high precision.

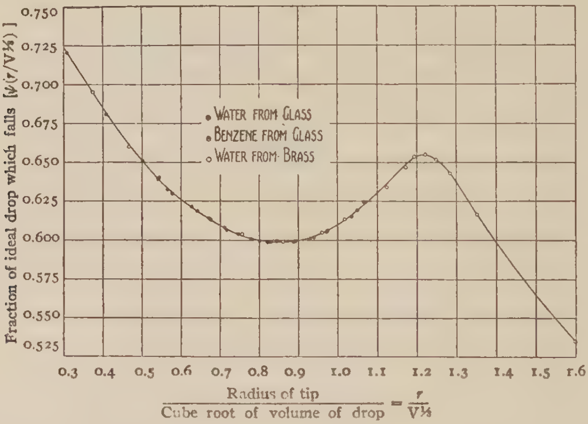

FIG. 27.—Relation between Radius of Tip and Fraction of Ideal Drop which Falls.

Since r is a linear dimension of any hanging drop, it is evident that if l is some other linear dimension of the drop, r/l will remain constant if the form of the hanging drop is kept constant while its volume is changed. In place of l, the cube root of the volume of the drop ($V^{1/3}$) may be taken. Now if the form of the hanging drop determines what fraction of it will fall, then the actual weight of the falling drop is

$$W = 2\pi r\gamma \,.\, f'(r/l) = 2\pi r\gamma f\,(r/V^{1/3}) \tag{4}$$

The square root of the capillary constant is a, and this acts as a linear dimension of the drop, so

$$W = 2\pi r\gamma f'(r/a) =$$

TABLE XIV

Drop-weight Surface Tension Corrections Which May Be Used Directly Without the Necessity of Employing Approximation Methods *

(Factors for division $= f\left(\frac{r}{V^{\frac{1}{3}}}\right)$ factors for multiplication $= \phi$)

$r/V^{\frac{1}{3}}$	$f\left(\frac{r}{V^{\frac{1}{3}}}\right)$	ϕ
0.00	(1.0000)	(1.0000)
0.30	0.7256	1.3780
0.35	0.7011	1.4263
0.40	0.6828	1.4645
0.45	0.6669	1.4994
0.50	0.6515	1.5349
0.55	0.6362	1.5718
0.60	0.6250	1.6000
0.65	0.6171	1.6205
0.70	0.6093	1.6412
0.75	0.6032	1.6578
0.80	0.6000	1.6667
0.85	0.5992	1.6688
0.90	0.5998	1.6672
0.95	0.6034	1.6572
1.00	0.6098	1.6398
1.05	0.6179	1.6183
1.10	0.6280	1.5923
1.15	0.6407	1.5608
1.20	0.6535	1.5302
1.225	(0.6555)	(1.5255)
1.25	(0.6521)	(1.5335)
1.30	(0.6401)	(1.5622)
1.35	(0.6230)	(1.6051)
1.40	(0.6033)	(1.6575)
1.45	(0.5847)	(1.7102)
1.50	(0.5673)	(1.7627)
1.55	(0.5511)	(1.8145)
1.60	(0.5352)	(1.8684)

* For single liquids it is usually best to use tips such that $r/V^{\frac{1}{3}}$ lies between 0.759 and 0.95.

Note.—All of the liquids tested give the same values of $f\left(\frac{r}{V^{\frac{1}{3}}}\right)^{\frac{1}{3}}$, which indicates that the considerable variations in density and viscosity had no detectable influence upon the value of the function. Within these limits this indicates the justification of the assumption that with any definite form of drop, no matter what its size, a definite fraction of material of the total drop is found in the drop which falls.

A considerable amount of accurate experimental work with the drop weight method has been done by Morgan and his associates, but all of his data will have to be calculated to surface tension values by means of the above table before they are available for use. These calculations are now being made by T. F. Young and the writer.

so since $W = mg$

$$\gamma = \frac{mg}{2\pi r \,.\, f\left(\frac{r}{V^{\frac{1}{3}}}\right)}$$

$$= \frac{mg}{2\pi r \,.\, f'\left(\frac{r}{a}\right)}$$

$$= \frac{mg\varphi}{2\pi r}$$

Here f represents a function of $r/V^{1/3}$, and f' represents a function of r/a. Values for the former function are given in Table XIV and Fig. 27.

If the vapor is dilute it is simplest to let m represent the weight in grams of one drop as weighed in air. Now since the drop as it hangs is also in air, no additional correction for buoyancy needs to be made. All that is necessary to do to determine the surface tension of a liquid is to determine the mass of one drop, calculate its volume (v) by dividing by a roughly determined density, also in air, calculate $v^{1/3}$, look up the value of f, and divide the value of mg by $2\pi rf$. The density of the liquid is involved only in determining the value of the correction which is not very sensitive to density differences.

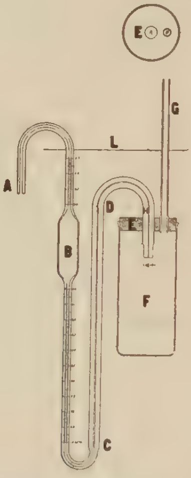

Fig. 28.—Dropping pipette for the determination of interfacial tension by the drop-weight-volume method. Suction is applied at G. E is a glass stopper in F, the vessel which contains the non-aqueous phase into which the tip extends. Usually a smaller vessel is used inside F in order to reduce the volume of the non-aqueous phase as much as is desired. B is the bulb of the pipette. Above and below this the stem is graduated in hundredths of a cubic centimeter so that it may be read to thousandths. The whole apparatus is mounted on a firm sheet of metal which holds a shelf and level above, and this is supported by heavy nickel-plated iron rods from a one-inch rod screwed into a heavy tripod with a base about 20 inches in diameter.

25. The Drop-Weight Volume Method for Interfacial Tension

The drop-weight method is directly applicable to the determination of the interfacial tension of mercury against water or an organic liquid, but for general use the drop-weight volume method as used in this laboratory is usually preferable. The apparatus is shown in Fig. 28. It is supported in the thermostat by a metal or hard rubber back. After equilibrium has been established the aqueous phase is put into the pipette $ABCD$. The tip is then placed under the surface of the other phase which is kept in F, or better in a vessel supported in F. The edge of the aqueous phase is drawn exactly to the end of the capillary at the tip, and the reading of the meniscus of this phase above the bulb of the pipette is taken. Suction is applied carefully at G, and drops are pulled off until the meniscus falls to the scale below the bulb. From the volume thus obtained the surface tension may be calculated by equation of the preceding section, which takes the form:

$$\gamma = \frac{V(d - d')g}{2\pi r f r / V^{\frac{1}{3}}}$$

$$= \frac{V(d - d')g\Phi}{2\pi r}.$$

The corrections involved are the same as those of the drop-weight method as given in Table XIV.

It may be noted that the phase which best wets the tip should be the one to be dropped either downward or upward into the other phase; if upward the capillary must be bent so that the face of the tip is upward instead of downward. Thus an aqueous phase is dropped downward into an organic phase of lesser density, or upward into one of higher density.

26. The Drop Weight or Drop Volume Method for Rapid Work, and for Small Amounts of Liquid

It is often necessary in industrial work to determine the surface or interfacial tension quickly, and sometimes only small quantities of material are available. To meet these requirements it is only necessary to use what seems to be entirely obvious modifications of the drop method. Thus the surface tension may be determined from the weight of a single drop, and often with an accuracy of a few tenths of a per cent. After the proper temperature has been attained, an essential procedure with any method, a single drop may be taken from the tip in less than two minutes, so the time is short, and the determination may be made by the use of only a few drops of a rare material. Similar modifications may be made in the drop-weight volume method. The surprising lack of understanding of the drop method is illustrated by an altogether incorrect criticism of the method by a well known worker, who stated that the method is not applicable to approximate or commercial work, since it would be impossible to spend five minutes per drop and still obtain the several hundred drops essential to the method. Evidently he had in mind the altogether erroneous method of the "drop number," that is, counting the usually large number of drops in a certain volume. Commonly the results are given in terms of the drop number, with the statement that this gives the correct *relative* values: a statement which is very far from the truth. A careful determination made with one drop gives a result of a very much higher order of accuracy.

27. Standards for Surface Tension

The present standards for surface tension are those established at 20° for water, 72.80 dynes per cm., and for benzene, 28.88. These values were established by independent measurements of the capillary heights by Richards, Carver, and Coombs,[38] by Harkins and Brown,[37] and by Harkins and Davies. The agreement between the different sets of measurements is extremely close, which was to be expected, since extreme precautions were taken to avoid all known sources of error. Very accurate work, but not of the same high order of precision, has been done upon water by Volkmann, by Domke, and by Sugden.[39] The latter obtained the value 72.70 for water by the capillary height, and 72.90 by the bubble pressure method, or a mean of 72.80.

Unpublished work by Young, Gross, and Harkins indicates that between 10° and 60° C. the surface tension of water is given with a high degree of accuracy by the equation:

$$\gamma = 75.796 - 0.145\,t - 0.00024\,t^2$$

in which t is the Centigrade temperature. The best data for benzene are represented between 20° and 60° by the equation

$$\gamma = 31.556 - 0.135\,t + 0.00006\,t^2.$$

Energy Relations at Surfaces *

The interfaces [20] commonly called surfaces are of several kinds: liquid-vapor, liquid-liquid, liquid-solid, and solid-solid. The thermodynamics of saturated films has been treated by Dupre,[3] Lord Rayleigh and more thoroughly by Gibbs [4] and by Einstein.[49] The following treatment is somewhat different from that presented by any of these workers, and has some advantages:

The surface film may be either saturated or unsaturated, and a part of the treatment presented will be applicable to either case.

Let $S =$ the entropy of the whole surface, s of unit area.
$U =$ intrinsic energy of the total surface.
$u =$ the intrinsic energy of unit area $= E_s$.
$\gamma =$ the free surface energy per unit area, or the surface tension per unit length.
$c =$ the specific heat of the surface, where specific refers to unit area and not to unit mass.
$A =$ the area of the film.
$l =$ the latent heat of the surface per unit area.
$Q =$ the total heat added to the surface.

These quantities may be thought of as applying to a film of infinitesimal thickness, but since this is not the true thickness for the actual film, they represent the surface densities. Thus U, as Gibbs states, denotes the excess of the energy of the actual mass which occupies the total volume considered, over that energy which it would have if on each side of the surface the density of energy had the same uniform value quite up to that surface which it has at a sensible distance from it.

From the first law

$$dQ = d(Au) - \gamma\,dA = A\frac{\partial u}{\partial T}\,dT + \left[A\,\frac{\partial u}{\partial A} + (u - \gamma)\right]dA \qquad (1)$$
$$= C\,dT + l\,dA.$$

This equation is perfectly general.

To be entirely exact a term which gives the work done by the expansion or contraction against the external pressure when material from inside the liquid goes into the surface, so

$$dQ = d(Au) - dA + pdv$$

Since h, the heat function, is equal to $u + pv$, and at constant pressure $dh = du + pdv$, the substitution of h for u in the equations which follow makes them exact. However, it is easy to show that the term pdv may be neglected, at ordinary pressures.

We will define c as follows:

$$c = \frac{1}{A}\left(\frac{dQ}{dT}\right)_{dA=0} = \frac{du}{dT} \qquad (2)$$

Equation 1 now becomes:

$$dQ = Ac\,dT + l\,dA = AC\,dT + (l + \gamma)\,dA - \gamma\,dA \qquad (3)$$

Let the film be saturated, and the definition of a saturated film will be that u and γ are functions of T only.

$$d(Au) = A\frac{du}{dT}\,dT + u\,dA = Ac\,dT + (l + \gamma)\,dA \text{ is an exact differential,} \qquad (4)$$

---

* This section was written by the author in 1916, and is quoted from a paper printed in 1917.

$$\text{and } c,\ l = f(T) \text{ only.} \tag{5}$$

$$c = \frac{\partial}{\partial T}(l + \gamma) = \frac{du}{dT}. \tag{6}$$

$$u = l + \gamma. \tag{7}$$

$$l + \gamma = \int c\, dT \text{ and is a definite function of } T. \tag{8}$$

From the second law

$$dS = \frac{dQ}{T} = \frac{Ac}{T}\, dT + \frac{l}{T}\, dA \text{ is an exact differential.} \tag{9}$$

$$\frac{c}{T} = \frac{\partial}{\partial T}\left(\frac{l}{T}\right) \quad \text{or} \quad c = \frac{\partial (l/T)}{\partial \ln T} \tag{10}$$

Combine (6) and (10), and

$$T\frac{\partial}{\partial T}\left(\frac{l}{T}\right) = \frac{\partial}{\partial T}(l + \gamma), \tag{11}$$

or

$$\frac{\partial l}{\partial T} - \frac{l}{T} = \frac{\partial l}{\partial T} + \frac{\partial \gamma}{\partial T}.$$

or

$$l = -T\frac{\partial \gamma}{\partial T} = -\frac{\partial \gamma}{\partial \ln T}. \tag{12}$$

Equation 7 now becomes

$$u = (\gamma + l) = \gamma - T\frac{\partial \gamma}{\partial T}. \tag{13}$$

$$c = \frac{\partial}{\partial T}\left(\gamma - T\frac{\partial \gamma}{\partial T}\right) = \frac{\partial \gamma}{\partial T} + \frac{\partial l}{\partial T} = \frac{\partial l}{\partial T} - \frac{\partial l}{\partial T} - T\left(\frac{\partial^2 \gamma}{\partial T^2}\right)$$

or

$$c = -T\left(\frac{\partial^2 \gamma}{\partial T^2}\right). \tag{14}$$

Equation 1 is fundamental for saturated and unsaturated surfaces, and Equations 13 and 14 for saturated films.

The experimental results indicate that over moderate ranges of temperature γ is a linear function of the temperature, or $\frac{d\gamma}{dT} = k$. So long as this is true u, the total surface energy per unit area, is independent of the temperature. This constancy of u makes it a very much more characteristic function than either the free surface energy or the latent heat of the surface (1). Tables of data show that, indeed, the total surface energy is not only largely independent of temperature, but is also very characteristic of any special class of compounds. In so far as γ deviates from a linear function u will vary with the temperature, so that even a greater regularity might have been obtained by calculating u from data taken at corresponding states. However, the regularities in the values of u as they have been obtained are extremely striking.

So long as $\frac{d\gamma}{dT}$ is a straight line, c, which is equal to $-T\frac{d^2\gamma}{dT^2}$, is zero; or the superficial specific heat is zero, as was found by Einstein. This indicates that *under this condition* all of the energy of formation of a surface ($= u$ or $\gamma + l$) goes into the surface in a potential form, and this in turn seems to show that the energy is stored up by some configuration of the surface layer. The fact that the total surface energy is almost independent of the temperature indicates that this configuration is almost the same for various temperatures, but it is quite likely that there may be some change in the relative distances of the molecules due to thermal expansion. Although thus far what we have found agrees well with the ideas of Einstein, our other results do not so well agree with a generalization which he introduces, that for every atom in the molecule there is a field of molecular attraction which is independent of the manner in which it is joined to other atoms, and that the summation of all these atomic attractions determines the free surface energy.

If we now imagine that inside a liquid plane area of 1 sq. cm. exists, and then pull the liquid apart over this area, so that two surfaces each 1 sq. cm. in area are formed, then the increase in free energy is 2γ. Now Equation 13 shows that at the same time there is a cooling of the surface equal to $2\,l$, so that the kinetic energy of the molecules aids in pulling the surfaces apart. The total energy $2u$ involved in this process may be imagined to be used up, (1) in giving orientation to the two sets of molecules on both sides of the imaginary plane, while still in the liquid, and (2) in pulling the two oriented surfaces apart. By this it is not meant that the process takes place in this order, but only that the end result is the same as the result of these two steps. While we have at present no way of determining the relative amounts of energy involved in the two steps, it would seem that the amount of energy involved in (1) is relatively small, and that the greater amount is that of step (2). Now, if we knew the laws according to which the electromagnetic forces vary in the fields between and in the molecules which make up the surface layers, it would be possible to get a solution of our problem. However, since this is not known, it seems better to solve the converse problem, that of determining the rate at which these forces fall off, from the data on surface energy.

Equation 12 indicates that if the free surface energy decreases with the temperature, as is usually the case, the formation of the surface will have a cooling effect, while if it increases with the temperature, as it does in the case of the two anisotropous liquids, ethyl *p*-azoxybenzoate, and ethyl *p*-ethoxybenzalamino-α-methyl-cinnamate, there will be a heating effect. In either case the first effect is to increase the free surface energy. It is evident that a contraction of an ordinary surface lowers its tension, and that the free surface energy of a fresh surface, between two phases which may exist together, is greater than that of an old one. If a surface is thought of as being formed with infinite speed, then the changes which follow are such as to lower the free energy.

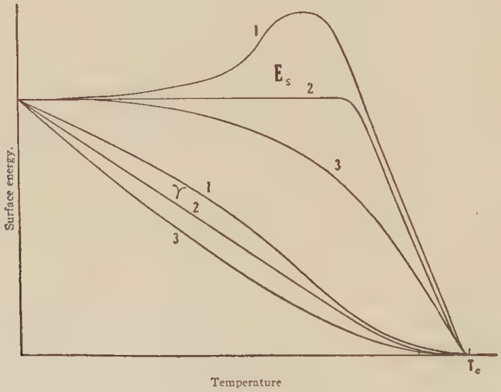

FIG. 29.—Variation of the free and total surface energy with the temperature, with three types of curves.

From thermodynamics we learn that the arrangement of the molecules in the surface of a liquid must be such as to make the free surface energy (γ) a minimum. Now, since

$$\gamma = u - Ts, \tag{15}$$

and when the change is not isothermal T changes, and when the change is not reversible the superficial entropy (s) changes, the condition for an isothermal reversible change in the surface is that there shall be a decrease in the total superficial energy (u) just equal to that of the superficial free energy (γ), so under the given conditions the configuration must be such as to make the total surface energy a minimum.

According to Jaeger, if curves are plotted with γ as the vertical axis, and with T horizontal, the curves are of three types, all of which slope rapidly downward as the temperature increases. The most common type of γ, T curves is type 3, which is convex toward the T axis. If we assume that all of the three curves begin at the same point on the γ axis, and end at a common point on the T axis, the curves take the form given in Fig. 29. The curve representing the total surface energy is given by Curve *3a*. This curve at first slopes gently, and finally rapidly downward when the γ curve becomes almost parallel to the T axis. When the curve is linear the total energy remains constant until this curve becomes convex to the T axis, when the u curve falls very rapidly. It will be seen that the type 1 curve for γ must change into a type 3 curve before it reaches the T axis.

These relations indicate that the specific heat of the surface is not wholly independent of the temperature, and that it approaches zero with extreme rapidity as the critical temperature is approached, so the surface film thickens rapidly and rapidly loses the orientation of its molecules just before the critical temperature is reached.

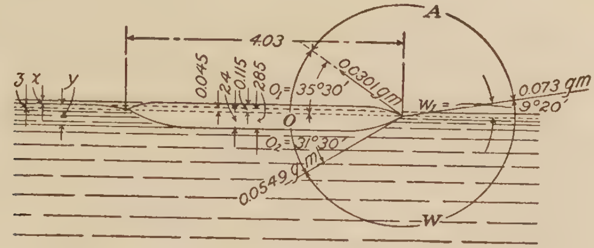

Fig. 30.—Vertical section of a lens of paraffin oil floating on the surface of water.

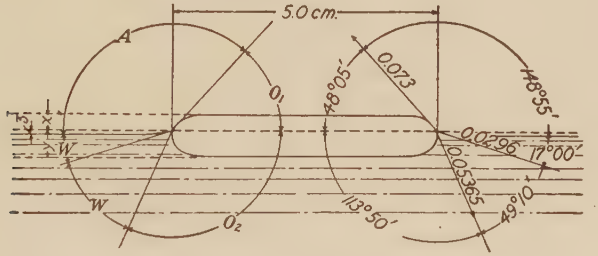

Fig. 31.—Vertical section of a globule of water floating upon carbon tetrachloride.

25. The Form of Floating Drops

Coghill and Anderson have made an interesting study of the form of floating drops. Fig. 30 shows the contour of a drop of paraffin oil on water, and Fig. 31 that of a drop of carbon water floating on carbon tetrachloride.

26. The Electrical Charges on the Surfaces of Colloidal Particles

Since atoms consist of particles which are negatively or positively charges, all surfaces are made up of electrical charges. Since electrons in general form the outer part of atoms, they also form the outer part of surfaces, with the exception that it is possible that the hydrogen ion or proton of the hydrogen in organic substances, water, etc., may also get into the extreme outer surface. However the relative positions of the proton and the valence electrons which bind it are unknown. A surface is said to be charged only when there is more electricity in it of one sign than corresponds to electrical neutrality. Such a charge reduces the surface tension. Such surface charges are of extreme importance in connection with problems relating with surface energy, but are not considered in detail in this section because they are discussed in a number of other sections of the book.

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Cohesion and Molecular Forces

By Sir William H. Bragg

This note is a very slight enlargement of an introduction to a joint discussion on cohesion and molecular forces held by Sections A, B and C of the British Association at its 1923 meeting at Liverpool. It must not be considered as an attempt to discuss the question of cohesion in any thorough manner, it is no more than an attempt at a sketch from the new point of view furnished by the methods of the X-ray analysis of crystals.

The analysis suggests that the very strong forces between atom and atom, molecule and molecule are limited in their effective line of action to distances much smaller than we have hitherto supposed; small, it may even be, compared to the distances between the centers of atoms as they lie side by side in a crystal. This does not mean that one atom cannot exert any influence on another some distance away, for such an action may be possible through the transmitting agency of intermediate atoms. There may be as it were a direct pull along a chain through the agency of intervening links. There may also be a transmission of influence through the sheer effect of arrangement, a kind of catalytic action, but the powerful direct forces which are the basis of cohesion would seem to be of extremely short range. We are led to picture one atom holding on to another at a point which is definite in the structure of each of them. In ionized solids, such as rocksalt, we have it is true to consider mainly electrostatic actions between center and center, but even then this cannot be the whole truth because there are directive tendencies in such bodies which seem unlikely to be due to electrostatic actions between atomic centers. The whole action of one atom on another cannot be explained in terms only of a central charge and a more or less rigid spherical envelope or of other properties or descriptions which are really equivalent to these.

A crystal conforms so exactly to rules respecting its angular dimensions that it seems impossible to imagine its form to be merely the result of an average of tendencies. The forces of adjustment cannot therefore be thought of as a force between two points each representing one of the molecules. On the contrary, it is nearer the truth to think that the adjustment is made so as to bring together certain points on one molecule and certain points on the other. In considering, therefore, the binding of the individual molecules of a solid, the analogy of the electrostatic attraction of two charged spheres is imperfect, and should be replaced by that of two members of a girder structure adjusted until the rivets can be dropped into the holes brought into true alignment. This is seen well in the recent work by Muller and Shearer, and by Piper and Grindley on the structure of the organic fatty acids and their salts. There is no doubt that the ultimate flakes of the crystals of these fatty acids are the monomolecular films investigated by Langmuir and by Adam, and it would appear that in passing from one acid to a homologue of greater molecular weight, each addition in thickness of the ultimate flake is made in complete independence of the previous length, as if the only thing that mattered was the nature of the attachment of one carbon atom to the next. There is no influence of the ends upon the atoms in the middle. Again, we have the forces different at different parts of the atomic surface, as in the case of bismuth and its homologues, in which the atom is attached to three neighbors on one side by bonds differing from those which attach it to its three neighbors on the other.

With regard to the nature of these binding forces three types may be recognized. First, there is the effect set up by the sharing of a pair of electrons by two contiguous atoms, leading to strong and directed attachment. Next, there are actions of a different and generally weaker type manifested in the binding of molecule to molecule in a crystal. We may be sure that this type plays an important part in metals and alloys. Lastly, there are the pure electrostatical central actions. In the case of the polar crystal Born and Landé have made some progress in calculating the effect of this type of force.

One well-known fact in crystal growth is that the faces have different rates of growth, indicating that there may be differences in the ease with which molecules slip into their places. Into this the element of time may enter, because a molecule may come nearly into its right place and be held there sufficiently long to get settled in by thermal agitation or otherwise. We may suppose that in some cases the formation of the crystal begins correctly enough, but that errors of adjustment creep in until the surface becomes somewhat disordered, and the growth ceases because fresh molecules cannot find their proper places to slip into. Without a more detailed knowledge of the active forces localized at various points of atoms and molecules we cannot build up a complete theory of cohesion.

Surface Tension of Colloidal Solutions and Dimensions of Certain Organic Molecules

By P. Lecomte du Noüy, Sc.D.

(From the Laboratories of The Rockefeller Institute for Medical Research)

A large number of papers have been published on the surface tension of colloidal solutions but, owing to the methods used, certain facts have been overlooked so far. The purpose of this paper is to review briefly the results obtained by using a different method, namely, the pull on a ring. By this method, the surface tension of the same layer of liquids may be measured, at intervals of time, instead of that of a continuously renewed layer.[1]

EXPERIMENTAL

It will suffice to say that the instrument used, based on the work of Weinberg,[2] has been described in the Journal of General Physiology,[3] by Sir William Bayliss,[4] and by Holmes.[5] The torsion of a wire controlled by a worm-gear is used to counteract the stress of the liquid film adhering to a platinum ring and, as the amount of torsion can be measured by a simple reading on a dial, the surface tension is measured directly. The measurements require only 20 seconds. Those reported in this paper were made at a temperature of 23 ± 0.5° C. Two cubic centimeters of liquid in watch-glasses were used, the diameter of the free surface being very nearly 4 cm. The glassware, containers, flasks, pipettes, watch-glasses, etc., were freshly boiled for 2 hours in a cleaning solution (sulfuric acid and potassium dichromate), rinsed in specially prepared distilled water, and dried. No alcohol or ether was ever used. When NaCl was used for preparing the solutions of serum, for example, it was washed, then recrystallized twice. The greatest care was taken in handling the solutions under experiment, so as not to disturb their surface. A special table was built on which the surface tension apparatus, supported on a small carriage, was rolled on rigid rails, in front of every solution in succession. Under such conditions, about 100,000 measurements were made and the following results, which will be summarized rapidly, were obtained:

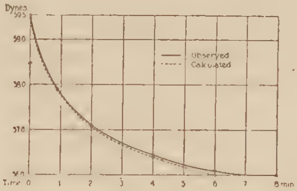

Fig. 1.—Drop of surface tension of pure blood serum (rabbit).

I. The surface tension of colloidal solutions is not constant but decreases rapidly in function of the time. So far, few colloidal solutions have been found which do not show this phenomenon. Experiments have been carried out mainly with blood serum, pure albumin, hemoglobin, globulins, sodium oleate, sodium glycocholate and taurocholate, and saponin solutions, a great number of dyes, and gold, silver, copper, and iron sols (electrically prepared). The drop varies, of course, according to the substances and to the concentration. It is much smaller in the electrosols mentioned above. At a given concentration, it can be roughly expressed by the formula (Text Figs. 1 and 2)

$$S = S_0 e^{-Kt^{\frac{1}{2}}}$$

until a certain stable value is attained. This phenomenon is due to the adsorption in the surface layer, in function of time, of the molecules in suspension. As the concentration of the solution in every watch-glass does not vary, this phenomenon seems to differ from ordinary adsorption which is considered as almost instantaneous. However, it may be assumed that in these colloidal solutions the concentration varies proportionally to the time as the adsorption progresses. This assumption is supported by the fact that the same formula, in which t is replaced by c (concentration), satisfactorily fits such adsorption isotherms as published by Lewis,[6] expressing the adsorption of sodium glycocholate by paraffin oil.

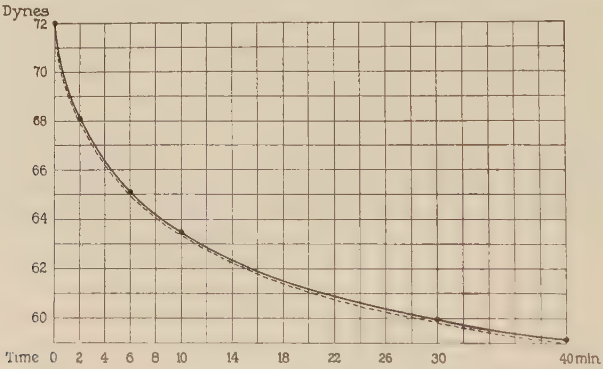

FIG. 2.—Drop of surface tension of a solution of 1/10 blood serum (rabbit). Dotted line is calculated according to the formula $S = S_0 e^{-Kx^{\frac{1}{2}}}$.

TABLE I

AGREEMENT BETWEEN FIGURES OBSERVED AND CALCULATED FOR THE LOWERING OF SURFACE TENSION AT THE INTERFACE BETWEEN A SOLUTION OF SODIUM GLYCOCHOLATE AND PARAFFIN OIL, IN FUNCTION OF THE CONCENTRATION (TEXT-FIG. 3)

$K = 0.222$

Concentration, *Per Cent*	0	0.1	0.2	0.3	0.4	0.5	0.6
Surface tension observed (Lewis) dynes	34.0	21.0	16.5	14.0	12.2	11.0	10.9
Surface tension calculated $(= {}_0{}^{e}{-KC^{\frac{1}{2}}})$, dynes	—	20.2	16.5	14.0	12.2	10.9	9.7

Text Fig. 4 gives an idea of the phenomenon in function of the concentration for a few substances. It is to be noticed that a sodium oleate solution in such quantities as 10^{-5}, although it affects the initial surface tension of water very little, will cause a drop of more than 25 dynes in 2 hours. The drop in the surface tension of sodium oleate at higher concentrations has been observed before, but could not be followed step by step on account of the methods used, and was not thought to be a general phenomenon of colloids. The effect of dilution was also overlooked. One hundred thousandth part of hemoglobin does not affect the initial surface tension of water, but causes a drop of 20 dynes in 2 hours. The drop weight or drop count methods are unable to show this phenomenon.

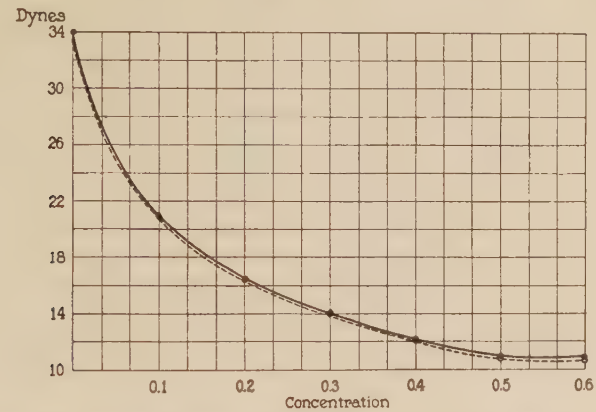

FIG. 3.—Action on surface tension of adsorption of sodium glycocholate by paraffin oil (Lewis).

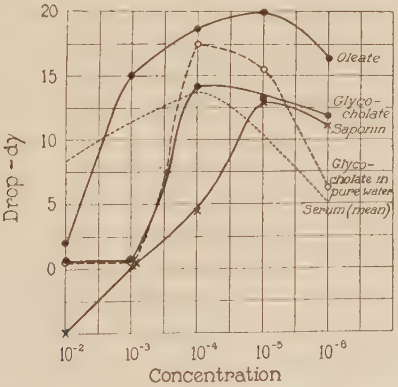

FIG. 4.—Time-drop of the surface tension of certain colloidal solutions, in function of their concentration.

II. In all the cases studied (organic colloids), a decided minimum value was observed at a given concentration. Under the conditions of our experiments, it occurred around 1/750,000 for sodium oleate, 1/140,000 for crystalline egg albumin, and 1/10,500 for rabbit serum and, as this serum contained 6.51 per cent of proteins, the final dilution was near 1/160,000. On both sides of this minimum (Text Fig. 5), the drop is smaller. In the case of certain strongly active substances (saponin, etc.), it often happens that, at low dilutions (1/10 to 1/1,000), a slight increase is observed instead of a drop. An hypothesis was made in order to account for the maximum drop. At this optimum concentration (the size and shape of the vessels in which the solutions were exposed being taken into consideration), the existence of a monomolecular and oriented layer was assumed; such a layer is only possible at one concentration in the same vessels, and its geometric organization would account for the existence of the smallest possible field of forces compatible with the

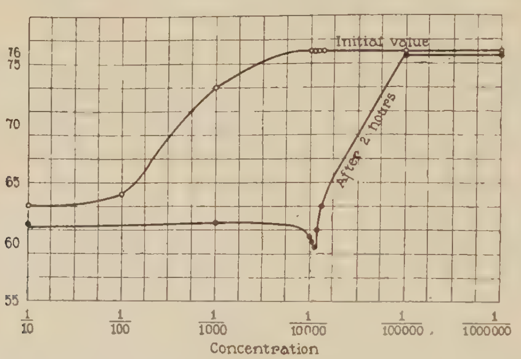

FIG. 5.—Initial values and values after 2 hours of the surface tension of solutions of serum.

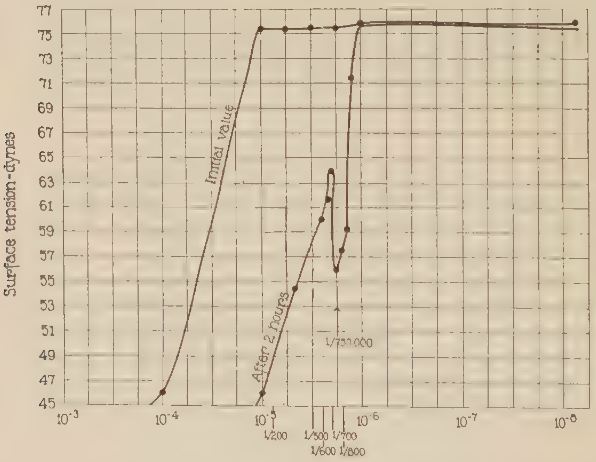

FIG. 6.—Initial values and values after 2 hours of the surface tension of sodium oleate solutions in water. Between 10^{-5} and 10^{-6}, the figures representing concentrations should be divided by 1,000, namely $\frac{1}{200,000}$, $\frac{1}{500,000}$, etc. Space did not allow more figures on the chart.

number of free molecules in the solution. Text Figs. 5 and 6 show how well defined and sharp this minimum is in the case of serum and sodium oleate. A more careful investigation on both sides of this minimum revealed the presence of two other minima. One of these probably corresponds to a monolayer (the writer proposes this term instead of "monomolecular layer") of horizontal molecules. Experiments are being carried out on this subject at present.[7]

III. If the solutions are stirred, even slightly, after standing, the surface tension rises and reaches a value generally smaller than the initial value (Text Fig. 7). This phenomenon can be repeated a number of times, and for this very reason great care must be taken when the time-drop is being measured. In the case of the biological colloids (blood serum) studied, after some time (48 hours), the solution became practically inert when it has been stirred frequently, and there was no further rise after stirring.

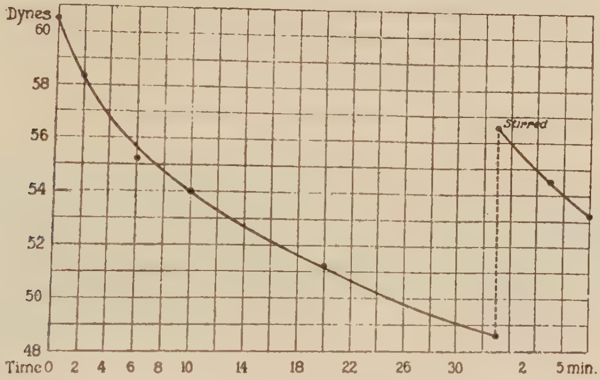

FIG. 7.—Rise in surface tension when solution is stirred.

IV. Should the above assumption of the existence of a homogeneous oriented monolayer at a given concentration be well founded, the rate of evaporation of such a solution should be slower than that of any other concentration. Water molecules would not escape so freely from a solution covered with such a film. At a higher concentration, we have assumed that there is a piling up, and no organization of the molecules. Therefore, the water molecules can pass between and escape more easily than through a closely fitting mesh of identically oriented molecules. At lower dilutions, the breaks in the film would allow the normal process of evaporation to take place. Experiments proved that, with the colloidal solution tested (blood serum), such was the case. The results of a series of experiments are given in Tables II and III.

TABLE II

DIAMETER OF SERUM SOLUTIONS (RABBIT) EVAPORATING IN WATCH-GLASSES

Dilution	10^{-1}	10^{-2}	10^{-3}	10^{-4}	10^{-5}	10^{-6}
Diameter in mm. at 5:41 P.M., after 6 hours' evaporation	26	27	27	30	27	26
30 minutes later	20	20	23	26.5	23	22
1 hour later	0	0	6	14	0	0

TABLE III

DIAMETER OF SERUM SOLUTIONS (RABBIT) EVAPORATING IN WATCH-GLASSES

Dilution	10^{-1}	10^{-2}	10^{-3}	10^{-4}	10^{-5}	10^{-6}
Diameter in mm. at 5:42 P.M.	18	23	21	21	20	20
50 minutes later	0	5	8	12	0	0

So far, our assumption seems to be supported by the facts. It is very plain in all these tables that solutions at 1/10,000 evaporated more slowly than the others. An interesting conclusion may be drawn from these experiments on serum. Of course, the critical concentration 10^{-4} is function, among other things, of the ratio $\frac{\text{surface}}{\text{volume}}$ of the vessels in which the solutions are exposed. In the case of our watch-glasses, this ratio is 13, if it is assumed that adsorption takes place on the glass, as will be shown later. Should the surface increase with respect to the volume (as happens when the volume decreases), this ratio would become very great. If we attempt to calculate the size of the vessels which would require pure serum to develop such a monolayer, in other words, in which the ratio $\frac{S}{V}$ would be nearly equal to 130,000 instead of 13 (the serum being diluted to 1/11,000), it is found that they would have to be of the order of magnitude of the blood capillaries, filled with blood cells. Thus, one of the factors governing the concentration of colloids in the serum is perhaps found. The adsorption of molecules of substances such as albumins and proteins in general (biological colloids) and sodium oleate takes place on the glass in a similar way as on the free air-liquid surface. This was ascertained in the following manner:

Two series of watch-glasses were prepared; in one series, 500 very small glass beads were placed side by side. The surface of the glass was thus increased by 14.2 sq. cm. The same set of solutions (rabbit serum at the following concentrations: 1/5,000, 1/6,000, 1/7,000, 1/8,000, 1/9,000, 1/9,500, 1/10,000, 1/10,500, 1/11,000, 1/11,500, 1/12,000, and 1/13,000) was placed in the two sets of watch-glasses. Without beads, the ratio equaled 12.8. With the beads, the volume of the liquid being the same, this ratio became 19.9. If our assumption is correct and provided adsorption takes place on the glass, the maximum drop must be shifted toward a higher concentration, and its place will be at a concentration $\frac{19.9}{12.8} = 1.56$ greater, namely, at 1/7,000 instead of 1/11,000. The experiments supported this view entirely, and the maximum drop, as well as the minimum value of the surface tension, occurred at 1/7,000 in the watch-glasses with beads.

The existence of such a criterion for a monolayer makes it possible to compute its thickness, if the concentration at which it occurs is accurately known. Text Fig. 5 shows that this value is very well defined. The specific gravity of anhydrous proteins of the serum was measured and found equal to 1.275. On such a basis, the thickness of a monolayer of blood serum was found to be 35.0×10^{-8} cm. The length of the molecule of crystalline egg albumin was found to be 41.7×10^{-8} and, if its molecular weight is assumed to be 34,000 (Sörensen), and Millikan's value for N, 6.06×10^{23}, is taken, we find the square root of the cross section of this molecule to be 29.2×10^{-8}.[8] Hence, it would seem to be oriented vertically. The same technique and calculation applied to a substance whose molecular weight is well known, such as sodium oleate, yielded the following figures: the minimum value of the surface tension occurs at 1/750,000, and the molecular weight is 304.35. The measured length of the molecule is found to be 12.3×10^{-8} cm., and the square root of the cross section, 6.8×10^{-8} cm.[7]

If we compare these figures to the dimensions of the molecule of oleic acid, as given by Langmuir (length, 11.2×10^{-8}; square root of cross section, 6.8×10^{-8}), we see that the diameter of the molecule is unchanged, but that its length is increased by 1.1×10^{-8} cm. When the length of insoluble organic molecules (oleic acid, tripalmitine, tristearin, cetyl palmitate, myricyl alcohol, etc.) is divided by the number of carbon atoms, the length per carbon atom is obtained. The mean value of this length, for 9 substances, is equal to 1.4×10^{-8} cm. As the sodium oleate molecule may be dissociated, a double electric layer is formed at the surface of the water, the free Na^+ ions being energetically attracted by the powerfully negative film due to the identical orientation of the oleic-ions in the surface layer. The experiments reported above bring a strong proof of the existence of true solutions of colloidal substances at high dilutions.

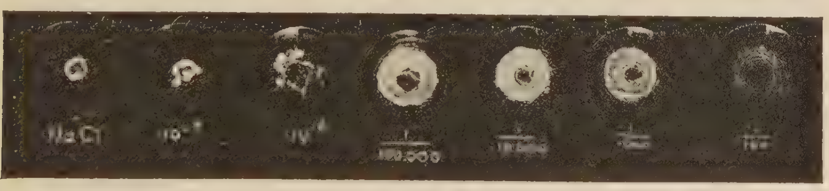

Fig. 8.—Crystals of pure sodium chloride; 2 c.c. of a 0.9 per cent solution in a watch-glass. (First watch-glass to the left.) In all the others a small amount of saponin has been added to a 0.9 per cent NaCl solution. The concentration of saponin is 10^{-2}, 10^{-3}, 10^{-4}, 10^{-5}, and 10^{-6}.

V. When a solution of NaCl (0.9 per cent) is allowed to crystallize in a perfectly clean watch-glass, the crystals are formed at the bottom and grow as evaporation takes place. They finally assume the appearance shown in Text Fig. 8 (to the left). When a small amount of any colloid is added to such a solution, concentration in the bulk no longer takes place, large crystals are not formed, and the sodium chloride (or any other salt of the same kind) is deposited on the walls of the watch-glass in a thin, smooth, and often opaque, white layer of very small crystals (Text Fig. 8). At the bottom, a darker area with a few tiny scattered crystals indicates that concentration did not take place, and that the molecules and ions are first being adsorbed on the colloidal micellæ, then carried up to the surface layer. As evaporation progresses, the colloidal particles, with their adsorbed NaCl, are deposited on the glass in concentric beaches. At certain concentrations, periodic rings are to be observed; at 1/100, for example, in the case of serum, and 1/1,000 for saponin and sodium oleate. The appearance of the crystals is quite characteristic of the concentration, and varies but little. Thus, in the case of a composite solution of colloids and crystalloids, Gibbs' law, which states that substances tending to increase surface tension will concentrate in the bulk, no longer holds true. This observation has thrown light on the spontaneous creation of membranes at interfaces which was difficult to explain before the discovery that not only colloids but also crystalloids concentrated in interfaces at the same time.*

VI. When two colloids are present in the same solution, one of the factors governing the final surface tension of the solution is the adsorption equilibrium existing between the two. The following experiment will make this clear. If a trace of powdered sodium oleate (about 1/10,000 in weight) is added to a less surface-active colloid in solution, such as proteins, gelatin, gum arabic, or metallic sols, the surface tension drops instantaneously by about 50 per cent, then immediately starts rising again until a certain equilibrium (which may be called adsorption equilibrium) is attained. In certain cases (pure blood serum, for example), the final surface tension is equal to the original value before the addition of sodium oleate. In order to observe this phenomenon, measurements must be made every 30 seconds, or at least every minute (Text Fig. 9).

The curve representing the phenomenon is again a logarithmic one. Let us call A the relatively inert colloid to which the surface active colloid B is added. When B is added in solution instead of powdered, or when the solution is stirred after its addition, the surface tension does not rise as high, as a greater number of micellæ of colloid A are coated with colloid B. When powdered sodium oleate (A) is added without stirring, a relatively small number of micellæ of colloid B are heavily coated with A, and in time practically all of A is adsorbed on a few B micellæ which either precipitate or collect in large aggregates with little action on surface tension. This buffing or antagonistic action of colloids seems to be a general phenomenon.

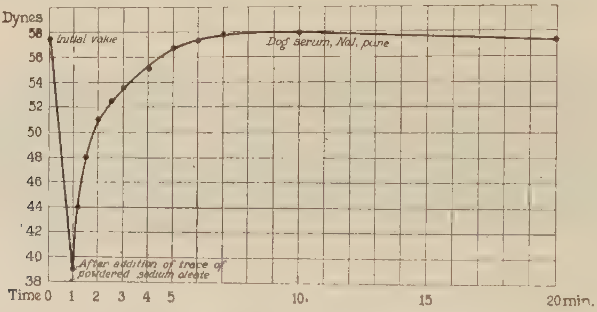

FIG. 9.—Recovery of the surface tension of a colloidal solution (rabbit serum, pure) to which a trace of powdered sodium oleate was added.

SUMMARY

The use of an instrument allowing measurements of the surface tension of the same layer of liquids at very short intervals (15 to 30 seconds) made it possible to study the evolution of certain surface tension phenomena in function of time, namely:

1. The spontaneous drop of the surface tension of all colloidal solutions, with the order of magnitude of 1 dyne per minute during the first minutes. This drop increases with dilution and shows a maximum at a given concentra-

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* On this phenomenon, see also paper by R. S. Liesegang, this volume. J. A.

tion, varying between 10^{-4} and 10^{-5} generally. The drop may then reach 20 dynes for colloids such as blood serum and albumin, which were not considered as acting powerfully on the surface tension of water. Certain colloids, saponin, for instance, do not show any drop at high concentrations but even a slight increase (10^{-1} to 10^{-3}).

2. When such solutions are stirred, the surface tension rises.

3. The existence of an accurate criterion of the existence of a monolayer at a well known concentration makes the calculation of the thickness of such a layer possible. In the case of pure soluble substances (albumins, etc.), it gives the length of the molecule and, when the molecular weight is known, its cross section can be calculated. The length of the molecule of sodium oleate was found to be 12.3×10^{-8} cm. and its width, 6.8×10^{-8} cm. The length of serum albumin was 35.0, and that of egg albumin 41.7×10^{-8} cm.

4. The crystallization of sodium chloride solution, or other salts, is affected by even the presence of one-millionth part of most colloids, and large crystals do not form at the bottom of a watch-glass. On the contrary, as the ions are adsorbed on the surface, the NaCl molecules are deposited in fine crystals along the walls of the glass, and form periodic rings at certain concentrations.

5. Evaporation of serum solutions in watch-glasses is slower at a dilution of 10^{-4} than at any other concentration. This fact is in favor of the assumption made in order to account for some phenomena reported above (1), namely, the existence of a monomolecular oriented layer at a given concentration.

6. When sodium oleate or any surface active colloid is added to another more inert colloidal solution, such as pure serum, for instance, the surface tension drops considerably, then rises immediately, and may reach its initial value in 7 minutes.

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7. Since this paper was written, a few other articles were published on the subject by the author, who was able to show that two other minima were observed in the case of sodium oleate, at the dilution: 1/1,220,000, corresponding to a thickness of 7.56×10^{-8} cm. and at the dilution 1/1,390,000, corresponding to a thickness of 6.64×10^{-8} cm. These are the three dimensions of the space occupied by a molecule of sodium oleate in a monolayer or a crystal. Thus, a very direct and simple way of calculating the number N of Avogadro was found by dividing the molecular weight by the mass of one single molecule. This gave the figure 6.004×10^{23}, differing by about 1% from Millikan's value. (*Phil. Mag.*, 1924, XLVIII, 664-672, and *Jour. de Physique*, 1925, Series VI, **4**, 145-153.)

8. The same method (footnote 7) applied to crystalline egg albumin (*J. Biol. Chem.*, 1925, LXIV, 595-613) made it possible to compute its thickness: 30.8×10^{-8} cm. from the experiment; and hence, to calculate its probable molecular weight, which was found to be 30,800, in satisfactory agreement both with the chemical composition and Sörenson's experiment.

Surface Films as Plastic Solids

By Robert E. Wilson

The theoretical and practical importance of surface films has long been realized, especially by those who have been working in the field of colloid chemistry. The great tendency has been, however, to consider the surface tension of the films and the concentration of the adsorbed constituents therein to be the only properties of the film which were of much importance. Recent work has shown, however, that variations in surface tension and concentration will not explain all the phenomena characteristic of solutions of colloidal substances. Thus two aqueous solutions of equal surface tension may differ greatly in the amount and stability of the foam produced when they are shaken. The same is true with regard to the relative stabilizing effect of different emulsifying agents.

Several British investigators[1] working several decades ago have demonstrated the existence of a rather high viscosity in the surface film. Upon consideration, however, it appears that even a high superficial viscosity could not account for the remarkable stability of some foams and soap bubbles. Thus Sir James Dewar kept large bubbles for nine months, taking precautions, of course, to prevent evaporation from the film.

In order to explain these anomalies in the behavior of surface films of various solutions, the writer was led to conduct an investigation of the physical properties and thickness of various types of surface films. The results appear to be of enough interest and importance to summarize them briefly in the following paragraphs.[2]

By studying the rate of damping of a torsional pendulum, the lower disk of which was immersed in the surface, it was proven that the surface films of some solutions possessed the characteristics of plastic solids rather than of viscous liquids in other words, their apparent viscosity increased rapidly as the rate of shear decreased, and there appeared to be a small but definite yield value which had to be exceeded before any flow whatever took place.

Good foam producers, such as saponin and sodium stearate, were found to give very strong plastic solid films and very stable bubbles, while sulfonated oil solutions of similar concentration and surface tension gave fluid films and relatively slight, unstable foams. Sodium oleate was intermediate between the two groups.

It was also found that the plastic solid films were of colloidal rather than molecular dimensions, and required a matter of hours to build up their maximum of thickness and strength. Some films were shown to have a thickness as great as 50 microns. The building up of these films was followed in a variety of ways, the most interesting of which was to focus a micrometer microscope on the surface of a solution containing some very fine suspended particles, and then following the plane at which solidification took place by watching the sudden cessation of Brownian motion as the solidification proceeded.

Solutions which form plastic solid films give erroneously high values for their surface tensions by the du Noüy and presumably by other methods of measurement, because the yield value of the plastic solid film is added to the true reversible surface tension.

In the case of liquid-liquid interfacial films, such as are known to be present in emulsions, there was considerable evidence of a similar behavior, although the results were not so clean cut. It was possible, however, to form irregular and even sharply pointed drops of one fluid medium in another in the presence of high concentrations of emulsifying agents which tended to give solid films.

In the case of liquid-solid interfaces the formation of plastic solid films has also been demonstrated in a variety of ways in connection with the problem of lubrication. Here again the films were shown to be of colloidal rather than molecular dimensions and to partake of the properties of a solid rather than of a liquid. Certain types of films were found to be strongly adsorbed and yet had very little lubricating value, while other films, such as those formed by stearic acid, produced a marked lowering in the static coefficient of friction between metal surfaces. The property of a lubricating oil to produce such adsorbed films and lower the coefficients of friction at slow speeds and under high loads is referred to as the "oiliness" factor of a lubricant and a variety of methods have been worked out for its measurement.[3]

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Molecular Association

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The Nature of Molecular Association

Speculation and study in regard to molecular association, using the term in its broadest sense, have formed the basis of the most fundamental conceptions in chemistry and physics during the last one hundred and twenty years. The conception of atomicity by Dalton and that of molecules by Avogadro were both concerned with processes of association or chemical combination. The further exploitation of these theories, particularly of that of Avogadro, based primarily on a study of gases, and later its extension to solutions, furnished to chemists during the 19th century the data for building our knowledge of chemical constitution and of atomic and molecular association and reaction.

Theories about the structure of the chemical elements are largely theories of association. Until past the middle of the 19th century, Prout's theory, projected in 1815, that the elements were derived from hydrogen as unit, was the subject of almost continuous discussion until Stas' precise work on atomic weights appeared to render the theory no longer tenable. Numerous modifications of it have subsequently appeared, amongst which we may instance that of Harkins.[1]

None of these newer theories, however, has claimed the attention which was fixed on Prout's hypotheses; for the human mind, in its craving for ultimate things, has in recent years received a measure of satisfaction in the results of the study of the electron and of radioactivity. Not only is the electron regarded as the structural unit of matter, but the derivation of elements of lower from elements of higher atomic weight has been explained as due to losses of α or β particles, corresponding, the former to a loss in mass, the latter to a change in electro-chemical character. In this way also, the existence of isotopes, slightly different varieties of the same element, has been recognized.

The forces which cause these units of matter to associate or combine may in all cases ultimately be electrical in origin; but it is possible to distinguish qualities or degrees of power in them marking different types of reaction. It is customary, indeed, to speak of chemical forces and of physical forces, according as one is supposed to be dealing with chemical reactions, such as between oxygen and hydrogen, and between calcium hydroxide and hydrochloric acid; or physical, as in the case of the solution of common salt in water. As chemical reaction itself may vary in intensity over a wide range, the line of demarcation is not easy to draw. The process of solution is clearly accompanied by the operation of chemical forces in those cases where the solute can crystallize out in union with definite molecular proportions of the solvent, as in the case of salt hydrates; in many other cases, where combination is not demonstrated by yielding a crystallizable compound, solvation is believed to occur, either the molecules of the solute or its ions, or both, becoming surrounded by and attached to, an envelope of solvent molecules.

The forces, which for convenience, we refer to as chemical, may expend themselves in stages. We now know, for example, that the oxidation of hydrocarbons passes through a series of stages. That of methane, for example, may be (1) $CH_4 + O_2 = H.CH(OH)_2$, (2) $H.CH(OH)_2 = H.CHO + H_2O$, (3) $H.CHO + O_2 = H_2O + CO_2$. The formation of many, if not of most compounds, may proceed in steps. The production of the stable compound does not mean, however, that the whole of the forces of any or each atom of the compound are completely satisfied or neutralized by those of other atoms. Berzelius recognized this fact in his electro-chemical theory of matter, and regarded the compound formed as polar, with an excess of either positive or negative electrical forces. Theories of valency, especially in this century, recognize polar forces or residual or contra valencies. Such residual forces may, like the outer lines of force acting between two electrically oppositely charged bodies, stray off into space and be ready to attach themselves to those of other substances.

A series of further actions and reactions, therefore, becomes possible. In the case of substances in which the ordinary valencies are supposed to be satisfied, we get further combination, such as between CO_2 and metallic oxides like CaO, or between NH_3 and HCl or ammonia and water, followed possibly by rearrangement of the atoms within the new molecule. We may also obtain so-called addition compounds like the salt hydrates and alcoholates or the periodides.

Another type occurs when two similar molecular entities such as NO_2, or H_2O, unite to form larger molecules, such as N_2O_4, $(H_2O)_n$; whilst a further type is seen in adsorption processes, as exemplified by the retention of small amounts of salts in colloids, the adsorption of small amounts of potassium permanganate by barium sulphate, the condensation of moisture, CO_2 and other gas films on solid surfaces.

The reactions due to these residual affinities differ in strength but are all related. It is of interest to note that probably all are influenced by the presence or absence of moisture. The latter is essential to the reaction between NH_3 and HCl and possibly to many others also. The breakdown of molecular complexes formed of similar molecules, such as molecules of nitrogen trioxide, is achieved by the presence of minute traces of moisture.[2] The power of adsorption shown by silica gel appears to depend on the presence of at least a minimum amount of moisture, whilst the adsorption of carbon dioxide by glass takes place all the more readily the less durable the glass, an easily weathered glass being one in which adsorption of moisture takes place to a marked extent.[3]

In a field which is so broad, the term molecular association as it is to be employed mainly in this paper needs delimiting. For our purpose, it has reference to the study of the variations in size which the molecules of any one substance can undergo without change of empirical chemical composition. In its broadest application, the molecular aggregate may be very large, may even indeed consist of a large crystal or of a globule or a micelle. At the other end of the scale we have molecules of smallest possible size, such as those of zinc, cadmium and mercury vapor which consist each of a single atom of the element; or of sodium chloride and potassium iodide vapors having a molecule corresponding to the simplest possible formula at high temperatures; whilst the molecules in sulphur vapor may range in size, dependent on the temperature and the pressure,[4] from S_8 to S.

The Forces Which Modify Molecular Size

We are thus brought to consider the subject of the forces which either break down or build up aggregates of like molecules. The simplest known processes for breaking down matter in the piece is to disperse it either in the ether in the form of a gas or vapor, or to dissolve it in some liquid medium. In these cases we obtain what may be described as a homogeneous distribution of the material in exceedingly small particles throughout the medium and the number of molecular units which comprise such a particle is either unity or a comparatively small number. Moreover, the particles in solution are either probably all of a size, or, when there are particles of varying size, the range, in practically all cases, appears to be small.

The other processes with which we are acquainted for procuring the dispersion of molecular aggregates do not yield particles so small or so uniform in size as does the process of vaporization or of solution. A dispersal corresponding in a sense to gasification occurs when solid matter is disrupted as in a violent volcanic explosion, the result of which is to scatter dust in an exceedingly fine state of subdivision through the atmosphere where it may remain suspended for a long period. Other terrestrial forces, such as wind, may bring about dispersal of particles already produced by winnowing fine dust from coarser and carrying it to considerable elevations. Reversal of the process, namely, gradually increasing aggregation caused in some cases by the electrical state of the atmosphere, brings about a settling out, just as invisible water vapor consisting almost initially of single molecules, forms mist and rain by condensation.

The formation of aerosols or smokes can be caused by various processes, including that of incomplete combustion. To quote a recent investigation, R. Whytlaw-Gray and J. B. Speakman, and J. H. P. Campbell have produced aerosols by the dissipation from electric arcs, of oxides of a number of metals, such as zinc, cadmium, aluminium, lead and magnesium. These aerosols initially contain particles of very varying size, including some of ordinary molecular dimensions. The average radius of the particles in the early stages was found to be 5×10^{-6} cm., with amicroscopic particles of radius 6×10^{-7} cm. with ZnO aerosol. Rapid settling out occurs, diminishing with time, until, after 5 hours, the settling is slow. The particles may produce flock-like aggregates in the case of certain oxides (ZnO, MgO, Al_2O_3) whilst others produce strings which, in an electrostatic field set themselves parallel to the field.[5] *

In liquid media, dispersal may be obtained by precipitation. Clearly, this is a process of condensation, in which the particles, initially of molecular size in true solution, are caused to coalesce and assume either visible size, as in the case of coarse-grained precipitates, or ultramicroscopic size in the case of sols, as examples of which we have the gold and silver hydrosols.

Dispersion in liquid media by a process similar to that used for obtaining the aerosols of metallic oxides is obtained by arc discharge under water, as in the formation of platinum hydrosols.

Fine grinding, especially in the presence of water, can lead to sufficient reduction in size as to produce plasticity in a number of non-plastic

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* See paper by W. Gibbs, this volume. J. A.

materials, like zirconia. The colloid mill carries this process through on a scale so efficient as to afford a practical method of preparing colloidal substances.[6]

Dispersion in the sense of emulsification can be obtained by agitation of the medium and the substance to be dispersed, especially through the influence of an emulsifying agent. Nordland[7] even obtained emulsions of water and mercury by shaking them together after the addition of a very small amount of potassium citrate to the water.*

As in the case of the aerosols, so also in the liquid sols, the size of the particles in the average sample varies widely, very large and very small particles being present. Sulphur, precipitated by the action of H_2S on an aqueous solution of SO_2 yields aggregates of widely varying size,[8] and the same is true of gold and other sols; but the actual range of sizes can be controlled by the concentration of the solution and by the action of electrolytes.

Methods of Measuring the Size of Molecular Aggregates

Having obtained a substance in a dispersed state, whether it be in the state of true solution or in the colloidal state, the question arises as to the methods by which the size of the dispersed molecules or particles may be measured. So far as colloids are concerned, the subject is dealt with in detail in other chapters in this volume where descriptions are given of methods of ultra filtration, ultramicroscopic and light scattering methods, including X-ray examination.

The connection between the ultramicroscopic particle and the molecule in its ordinarily accepted sense appears to have been established as the result of the study of the Brownian movement, the rate of diffusion and the rate of settling of particles in sols and the test as to whether the formula for the kinetic energy of a molecule, namely, $3/2 \frac{RT}{N}$ applies to sol particles. The value of N, known as the Avogadro constant, has been calculated to be 6.06×10^{23}, whilst Svedberg,[9] from diffusion experiments on a gold sol found $N = 5.8 \times 10^{23}$ and Perrin[10] obtained good agreement between the observed number of particles of gamboge distributed over planes at different heights in the suspension and the number calculated on the assumption that the above formula applied to them. The molecules in true solution and the particles in sols are, therefore, regarded as obeying the same laws and only being differentiated through size.

In studying the molecular size of substances in the state of vapor or in solution, the method adopted is based on Avogadro's hypothesis. In the state of gas or vapor, the relative molecular weight is obtained by a comparison of the density of the substance with that of oxygen; whilst, in solution, our problem is to determine what weight of the substance, dissolved in 22.4 liters of solution, will produce at 0° an osmotic pressure of 1 atmosphere.

Very few measurements of molecular aggregation in solution have been obtained by a direct determination of the osmotic pressure. In most cases, the result has been obtained indirectly, by measurement of the diminution of vapor tension or rise in boiling point, or the lowering of freezing point. Indeed, the methods most frequently adopted have been rather of an empirical character relying on Raoult's laws of solution.

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* Henri Moissan found that on adding a little platinum to mercury, the metal would emulsify when shaken with water. J. A.

MOLECULAR ASSOCIATION AND THE FACTORS WHICH INFLUENCE IT

As the main object of this article is to indicate the bearing of what we know about molecular association on colloidal phenomena, the author proposes to limit the discussion of the subject to gases or vapors and to solutions. Consideration of the liquid state is omitted.[11]

We propose to illustrate the fact that the molecular weight to be ascribed to a substance is subject to a variety of factors, namely, the nature of the substance itself, the nature of the solvent, the temperature and the pressure or concentration.

The behavior of the chemical elements when vaporized admits of fairly ready classification. The molecular weight, determined by comparison of the vapor density with that of oxygen, indicates that the molecules of the elements of Group O in the Periodic Table as well as those of such metals as have been tested consist of but a single atom, their molecular formulæ over the range of conditions to which they have so far been subjected, being correctly expressed by He, Ar, Ne, Xe, Ag, Zn, Cd, Hg, Th and Pb. The metalloids, on the other hand, arsenic, antimony and bismuth, have complex molecules, the complexity decreasing as the metallic characteristics are developed. Thus, whilst the values of the molecular weight of arsenic at 1700° were observed by Biltz and Meyer to be between 153.2 and 160.1, corresponding approximately to As_2, those for bismuth at 1640° were 214-244, or little more than corresponds to the formula Bi. The series may be completed by reference to phosphorus, in the same Periodic Group, which, between 800°-1700° has given molecular weight values varying from 111.3 to 92.1, or P_4 to P_3.

The permanent gases other than those of Group O, namely, oxygen, hydrogen and nitrogen have diatomic molecules over the whole range so far tested, a range of 2000° not being sufficient to cause change. Increase in the atomic weight is often accompanied by a tendency to simplification of the molecule. Thus, whereas chlorine between 0° and 300° appears to contain a mixture of Cl_2 and Cl_4 molecules, mainly Cl_2, and shows but slight indication of dissociation of the diatomic molecule at 1450°, the molecular weight of bromine at 1050° is but 150.5 (instead of 179.8 for Br_2) and that of iodine changes from 254 to 144 between 650° and 1400°. In the case of sulphur, we have an element of complex molecular formula, approximately S_8 at a temperature just above its boiling point, reduced at 1690-2023° to between S_2 and S.

Amongst compounds, some apparently have molecules of simple type, corresponding to the simplest possible formulæ, as, for example, NaCl, KCl, $ZnCl_2$, $ZnBr_2$, $HgCl_2$, $PbCl_2$, $CrCl_3$ and $CrCl_2$, whereas in other cases, the molecular weight at the lower temperatures investigated, indicates a double molecule, such as Hg_2Cl_2, Ag_2Cl_2, Al_2Cl_6, Al_2Bi_6, Al_2I_6, Fe_2Cl_6, $H_2P_2O_6$, N_2O_4, N_2O_6, P_4O_6, P_4O_{10}, As_4O_6, and Sb_4O_6. Water vapor contains a proportion of double molecules. With rise of temperature, in those cases investigated, the double molecule undergoes progressive dissociation. Thus, for arsenious oxide, the molecular weight at 518° corresponds closely to As_4O_6 whereas it is practically As_2O_3 at 1800°.

Reduction of pressure favors dissociation. At 850°, sulphur vapor at 100 mm. pressure contains a mixture of S_2 and S molecules whereas rise of temperature alone does not appear to bring about a similar reduction until 1600°-1700°.[12] The proportion of P_2 molecules in phosphorus vapor at 1300° also progressively increases from about 60 per cent to 89 per cent as the pressure falls from 760 mm. to 100 mm.

A further factor which influences molecular association not only in a pure liquid, but also in the state of vapor, is the presence of water even in minute amounts. H. B. Baker[13] has shown that not only may the melting point of sulphur, bromine, sulphur trioxide and benzene and the boiling point of nitrogen peroxide, nitrogen trioxide, methyl alcohol, benzene and ethyl ether be raised very substantially by rigorous drying for a period of years, but vapor density determinations made on ether and on methyl alcohol dried for 10 years indicated that the changes of boiling point were to be ascribed to the formation of more complex molecules both in the liquid and in the vapor. The vapor density of the rigorously dried ether was found to be 81.7 instead of that which corresponds to $(C_2H_5)_2O$, namely, 37, whilst instead of 16, the value for methyl alcohol corresponding to the simple formula CH_3OH, 45 was the experimental result. The latter figure would seem to indicate the existence of molecules of formula $(CH_3OH)_3$.

When benzene, dried for 10 years, was boiled, the thermometer when immersed in the liquid registered a temperature for the boiling point in excess of 105° (instead of 80°) whilst in the vapor, the temperature initially was 81° but rose to 87° at the close of the distillation. It is clear that the molecules constituting the liquid must either undergo dissociation or that the liquid is a mixture from which the simpler molecules distil first leaving portions of greater molecular complexity. In any case, it is an obvious deduction that dissociation occurred on passage from the liquid to the vapor state since at no stage of the distillation did the temperature of the vapor approach within 18° of that of the liquid.

Smits[14] has been led from these observations of Baker to a study of dried sulphur trioxide and phosphorus pentoxide in the solid state, and from the variation of vapor pressure during distillation together with the fact that melting takes place over a range of temperature, finds evidence that these substances (probably like the substances dried by Baker) are complexes in which the different molecular species may conceivably form mixed crystals with one another. Dynamic allotropy, arising from the conversion of one molecular complex into another, has previously been exemplified by liquid water and liquid sulphur and phosphorus.[15] Smits' work extends the idea to solids.

Passing on now to the subject of molecular sizes determined from a study of liquid solutions, the metallic elements dissolved in mercury or in tin appear to have molecules of atomic size in those cases in which combination does not occur between solvent and solute. Of the non-metallic elements, phosphorus and sulphur, in solution in carbon disulphide, and selenium in phosphorus are the only examples found having molecules greater than diatomic. Even in dilute solution, namely, 1.58 grams per 100 grams of carbon disulphide, the observed molecular weight of phosphorus was found by Beckmann to be 129 ($P_4 = 124$) increasing progressively with concentration to 170 at 18.86 grams per 100 grams of solvent. Similarly for sulphur the molecular weight over the range investigated corresponded to a molecular size of between S_8 and S_{10}.

Several oxides have been investigated, including water, the oxides of nitrogen, boric oxide, arsenious and arsenic oxides, and it has been found that nitrogen peroxide in acetic acid and arsenious oxide in nitrobenzene have molecules corresponding rather to N_2O_4 and As_4O_6 respectively than to the simple NO_2 or As_2O_3, whilst the existence of molecules greater than corresponds to the formula H_2O is also indicated in a number of investigations.

The actual molecular weight determined depends on a series of factors, just as does the molecular size in the state of vapor, and it is more satisfactory to deal with the subject from the point of view of these factors.

The molecular complexity depends, as above stated, on the nature and constitution of the substance in solution, on its concentration, on the temperature, and finally on the solvent itself.

The influence of the first factor is best illustrated by the organic compounds. Certain groupings in the molecule of these compounds appear to confer the power of forming molecular complexes; thus, the alcohols, phenols, carboxylic acids, amides, anilides, oximes in particular are liable in certain classes of solvent to have complex molecules, such, for example, as benzoic acid, acetic acid, acetamide when dissolved in benzene or ether or chloroform.

Electrolytes in solvents of low dielectric constant may form complexes several times the mass of the simple formula weight. For example, triethylsulphonium iodide, $(C_2H_5)_3$ SI, was found to give, in chloroform solution, for the range 5.7 to 12.5 per cent concentration, molecular weights ranging from 1765 to 2951, the highest number being twelve times approximately the value corresponding to the formula.[16] Both Walden and Turner have investigated a very large number of salts in solution and shown them to have the power of forming large molecular complexes.

An increase of concentration should, like rise of pressure in the case of a gas or vapor, favor the formation of complexes. Experiment fully bears out this effect, but the rate of variation of the molecular weight, even in any one solvent, varies with the substance; thus, ethyl alcohol shows a molecular weight progressively increasing from 64 to 148 for solutions in benzene ranging from 1.2 to 16.4 grams per 100 grams of solvent. On the other hand, acetic acid in the same solvent and for the concentration 0.34 to 14.1 grams per 100 of solvent, the molecular weight changes only from 100.8 to 123.6, that is to say, from a value somewhat less than corresponds to $(CH_3.COOH)_2$ to one a little more than the double formula weight. In other words, the increase of molecular complexity with increase of concentration varies from substance to substance. It has been suggested by certain workers, for example, by Auwers in connection with the aromatic acids, and by Wedekind and Paschke in connection with salts, that the double molecule represented the upper limit of complexity. Extended investigations, however, do not appear generally to justify these contentions.

In regard to the influence of temperature, comparatively few data are available, but in benzene as solvent benzoic acid at 5.5° has a molecular weight of 233, whilst at the boiling point, 80°, the value is 193. Again, in acetic acid at the same concentrations tetraethylammonium bromide[17] has an association factor of 1.63 at 118°, and 2.51 at 16.6.

The nature of the solvent very largely determines the molecular complexity of the substance dissolved in it. This influence may be of a definite chemical character leading actually to compound formation. In such cases the interpretation of the results of determinations is not always easy to give, but the various types of result have been classified by W. E. S. Turner.[11] In cases where combination is not known to occur the all important factor is the dielectric constant of the solvent.* In very general terms it may be stated that molecular association is hindered in solvents of high dielectric constant and permitted in solvents of low dielectric constant. Indeed, for any particular substance at a fixed temperature and concentration the molecular complexity of those substances which have any tendency to complex molecules is a function of the dielectric constant.

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* See paper by J. Errera, this volume. J. A.

In the case of organic compounds this statement may be illustrated by reference to the work of Meldrum and Turner [18] on the amides and anilides, the following table summarizing the results for five different solvents:

Solvent	Alcohol	Acetone	Chloroform	Ether	Benzene
No. of amides investigated	28	27	22	14	21
No. of amides which form simple molecules	24	20	4	5	4
No. of amides which form associated molecules	4	7	18	9	17
Dielectric constant of solvent	18.0 at 78°	17.0 at 56°	4.13 at 61.2°	4.12 at 35°	2.3 at 80°

In like manner the molecular weight of acetic acid and of benzoic acid in a variety of solvents increases as the dielectric constant of the solvent diminishes. The connection in these two last cases is to be regarded as general rather than quantitative, especially in view of the fact that benzoic acid appears to be associated to a marked degree in water.

The same general connection between the dielectric constant and the degree of molecular complexity is shown by electrolytes. The following table, containing the results for two electrolytes, will suffice to give an indication of the nature of the relationship, the electrolytes selected being diethylammonium chloride and tetrapropylammonium iodide. The concentration of the solution selected as standard is that of a comparatively dilute solution.

Solvent	Temp. of Expt.	Dielectric Constant	Degree of Association at Concn. 25 Milligram Mols. per 100 C.C.	
			$(C_2H_5)_2NH_2Cl$	$(C_3H_7)_4NI$
Water	100.0°	66.0	0.61	0.65
Formic acid	16.0°	58.5	0.68	0.73
Nitrobenzene	6.0°	40.0	—	0.81
Acetonitrile	87.5°	31.7	1.68	0.60
Ethyl alcohol	78.0°	18.0	1.00	0.98
Acetone	56.0°	17.0	—	1.15
Sulphur dioxide	20.0°	14.0	1.41	—
Urethane	60.0°	13.6	1.27	1.09
Phenol	48.0°	9.7	1.24	1.34
Pyridine	116.0°	9.5	1.83	—
Dimethylethylcarbinol	102.0°	7.9	1.24	—
Acetic acid	19.0°	6.3	1.63	—
iso-Amyl alcohol	132.0°	5.7	1.48	2.12
p-Toluidine	44.0°	5.4	1.55	1.33
Bromoform	8.0°	4.58	3.03	—
Chloroform	61.2°	4.13	2.53	4.20
Diphenylamine	52.0°	3.3	1.98	4.46

Some of the association factors are influenced by chemical action between the solute and the solvent, but in general it is clear that in solvents of high dielectric constant there is marked dissociation, whilst in solvents of low dielectric constant there is pronounced association. Which of the two phenomena will be observed, namely, electrolytic dissociation on the one hand or the formation of large molecules on the other, depends on the influence of the solvent.

The Molecular Complexity of Colloidal Substances

Part of this paper has been devoted to indicating that it is possible to have a succession of particle sizes ranging from that which corresponds to the single or simple molecule, such as we have in many cases of ordinary solution, right up to large size particles, the identity and approximate size of which can be determined by processes such as ultrafiltration, or by the ultramicroscope. The studies of Perrin and of Svedberg, to which reference has already been made, appear to indicate that such gradation of sizes actually occurs without break. In other words, colloidal solutions are continuous with what we may describe as true solutions.

The results discussed in the preceding section indicate the difficulty of attempting to ascribe a fixed formula to many substances since the size of the molecule depends on quite a number of factors, and it is impossible to prescribe a standard set of conditions under which the molecular size of different substances can be measured. The writer has previously indicated[13] that in colloidal solution phenomena are observed which may possibly with profit be compared with those described in the preceding sections. Molecular weight determinations carried out with colloidal substance in water such as the following, based on diffusion experiments, clearly indicate very high values.[19]

	M. Wt.
Gum arabic	1,750
Tannic acid	2,730
Egg albumen	7,420
Caramel	13,200

It is very interesting in this connection to recall the behavior of certain amides and anilides which were found by Meldrum and Turner[20] to possess exceptionally high molecular weight in water, and therefore, to be an apparent marked exception to the rule connecting molecular weight and dielectric constant; and the somewhat similar results obtained by Peddle and Turner[21] according to which they showed that out of 28 organic substances examined, 16, including butyric, benzoic and salicylic acid, several phenols and amines were distinctly associated even in dilute aqueous solution. Although not true of all cases, it was found that only weak solutions could be obtained of a number of the substances which exhibited marked association in water suggestive of such substances as ferric hydroxide, silica, white of egg, etc., which are insoluble in the ordinary sense in water, and apparently give rise to large molecular aggregates.

In this same connection we may consider the influence of the dielectric constant of the solvent. Many electrolytes which are readily soluble in water and have an apparent molecular weight in aqueous solution much smaller than corresponds to the formula weight are insoluble in solvents of low dielectric constant. Those electrolytes which do dissolve, such as the salts of organic ammonium bases, give rise to molecular complexes. Other electrolytes, however, which do not yield ordinary solutions may be made to produce colloidal solutions, such, for example, as of sodium chloride in benzene. The colloidal particles in such cases may be regarded as corresponding to great molecular complexity, and precipitation occurs when the complexity reaches a certain limit.

More recently somewhat similar views have been expressed by Walden[22] in connection with some determinations of degree of association of binary salts in different solvents. He pointed out, as the writer had previously shown, the successive increase in the degree of complexity of binary electrolytes with diminution of dielectric constant of the solvent. An extreme case occurred with tetra-amylammonium iodide dissolved in benzene and in carbon tetrachloride, the dielectric constant of these two solvents being 2.3 and 2.2 respectively. It was found that tetra-amylammonium iodide scarcely produced any appreciable rise of boiling point even in a 14 per cent solution, so that the molecular weight of the iodide must be exceedingly great. In his view solvents with dielectric constant of a value about 2 may be said to exercise a protective action on highly complex molecules and to maintain them at a size which is characteristic of colloids.

At the present stage of our knowledge it would be well to leave the foregoing remarks as suggestions rather than as definite statements.

A further suggestion may be made, however, namely, that it should be possible to link up the phenomena of colloids and of ordinary solutions by ultramicroscopic or by X-ray study of solutions of substances which form complex molecules in solvents of low dielectric constant. This is a field of investigation which, so far as the writer is aware, remains yet to be entered.

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Friction, Surface Energy, and Lubrication

Sir W. B. Hardy, Sec. R. S.

Two kinds of friction may be distinguished, the internal friction of fluids, usually called their viscosity, and the surface friction of solids, which, in contrast with internal friction, might be called external friction.

External friction is the resistance to relative motion which two solid faces in contact offer; it is the reaction to the traction on the interface, and there are two kinds, kinetic and static, according as the traction does or does not cause slipping.

Consider an external force applied to one of two masses in contact and growing gradually from zero. The tangential component produces a displacement at the interface which, though insensible in magnitude, brings into play elastic forces equal and opposite to itself, until a point is reached beyond which the forces evoked do not suffice to balance the traction, and slipping occurs. This point is a true yield point, and it is the point at which the elastic forces of reaction are at their maximum. Slipping cannot increase them unless the state of the material about the plane of slip is altered by the heat generated in the recovery from the strained state.

The position of the plane of slip seems to vary. It is in the solids when the faces are clean, and the faces themselves, therefore, are torn when slipping occurs. It is in the lubricant when the static friction is lowered sufficiently. Perhaps the true distinction between a lubricant and an abrasive is that the latter places the plane of slip within the solids.

External friction is subject to a law, formulated by Amontons in 1699, according to which the resistance to relative motion is independent of the area of the applied surfaces, and varies directly with the force, called the load, which presses them together.

Amontons' law may be put: For the same solids and the same lubricant, the tangential reaction (friction) per unit area is dependent only on the pressure. We now see why the area disappears. It occurs on both sides of the equation and cancels out. No simple explanation of this law is forthcoming. Like Hooke's law it is probably one of those laws of average values which mask the innate complexity of matter. It may perhaps be taken to mean that the reaction to the tangential stress includes a dilatation along the normal to the interface which is a constant fraction of the total strain.

In 1781 Coulomb confirmed the law and accepted Amontons' explanation of friction as being due to the engaging with one another (l'engrainage) of the asperities of the surfaces. This view still holds the field—it is still the orthodox view of the text book. At the limit it means that the free surfaces of solids are frictionless, a conclusion repugnant to modern conceptions of matter. Until near the end of the last century the most carefully polished surfaces were supposed to have somewhat the same kind of relation to the surface of a liquid that a ploughed field has to the most delicately polished mirror. Rayleigh,[15] and later Beilby, showed that a polished surface is free from such asperities as are here postulated. It is indeed formed by a true flowing of the material of the solid.

The origin of the forces which constitute the reaction of the surfaces is to be sought elsewhere than in the interlocking of material asperities. It is to be found in displacement of the centers of mass of the atoms, and in their rotation. At all surfaces there is a field of attraction like that which holds a drop of water to the end of a glass rod against gravity. When two surfaces are brought together there is mutual attraction. It is to this attraction that friction is due.

Consider two atoms on either side of the interface. They will attract one another and a tangential force applied to one of them will move its center of mass and also rotate it, and be resisted by the forces evoked by these displacements. The total reaction is the sum of all these individual reactions.

Friction is thus seen to be a phenomenon of particulate matter. There would be no friction at a surface between masses each of continuous homogeneous attractive matter. There would in general be static but not kinetic friction between two particulate masses whose particles were held in a lattice frame both regular and rigid. There would be both static and kinetic friction, however, if the lattice were elastic, for then relative motion would maintain a state of strain whose energy would always be in process of dissipation as vibrations of the particles.

The orientation of atoms and molecules is of peculiar importance in surface phenomena, because at surfaces the configuration of the atoms differs from that obtaining in the interior. In the interior of a crystal of ice, for example, each oxygen atom is surrounded by four hydrogen atoms and each hydrogen atom is attracted by two oxygen atoms, the former having given up their valency electrons to the latter. This disposition cannot hold at the surface where there must be oxygen atoms with less than four hydrogen atoms or hydrogen atoms bound to less than two oxygen atoms.

An atom at a free surface is attracted only in the inward half of a sphere described about it, whereas the attractive forces acting on an atom in the interior are distributed throughout the whole of a circumscribed sphere. There may, therefore, be said to be an excess of attraction at the surface the total potential of which, with the excess of heat in the surface layer, constitutes the surface energy.

The condition of least potential of a free surface is that the configuration should be such as to make the external attraction field as small as possible. The field may be taken to be less than that of an interior surface freshly laid bare by fracture. Whatever its relative strength, however, it is sufficient forcibly to attract other forms of matter—to condense vapors on to the surface, and to hold fluid against gravity. Why then do not two faces of similar matter, *e.g.*, two crystals of iron or of salt, weld when pressed together?

The answer is difficult. It is usual to rest content with vague references to the presence of a cushion of condensed gas which prevents contact. Probably three things are concerned. The cushion of gas, the layer of insensible thickness of material condensed from the atmosphere or derived from contact with other bodies, and the fact that the superficial configuration of the atoms of a solid differs from that obtaining at any imaginary surface in the interior in a way which reduces the attraction along the normal, the "free" attraction, to a minimum.

If friction be the sum of the tangential components of the resistance to displacement and rotation of atoms and molecules at or near the interface, it should bear some relation to the attraction along the normal to the interface, for that also will depend upon the configuration. There is direct evidence of this. Budgett[2] found that the force required to pull asunder steel plates which had been pressed together depended upon the nature of the contamination which had been applied to the faces. His breaking loads were, water 36, paraffin 26, and olive oil 19. The coefficient of static friction of steel faces lubricated with these substances is in the same order, namely, water .75, paraffin .4 and olive oil .07.

The film of contamination which covers solid surfaces, or at any rate the grosser part of it, can be removed by special treatment which varies for each individual substance, and the surfaces are then left clean. A "clean" surface, for reasons already stated, cannot be considered the same as a surface freshly exposed by fracture. Steel fractured under mercury is said to amalgamate. A "clean" surface of steel will not amalgamate.

Though the nature of a clean face is unknown, whether for instance, it is or is not always covered by a layer of condensed gas, it is a perfectly definite state in that it can be reproduced at will and identified by the friction. Plates of a certain kind of glass, for example, were "clean" when the coefficient of friction was .94, of steel when it was .74. No procedure would raise the friction above these values.

Clean faces not only have the highest static friction obtainable—they seize together and the cohesion of the original surfaces is stronger than that of the interior of the solids themselves which are therefore torn when relative motion occurs.[7]

All the experiments the results of which are described below were carried out with clean faces in pure air. It is not sufficient to remove the water vapor and greasy matter, care must be taken also to remove even the vapor of sulphuric acid if this be used to absorb water vapor.

Most substances will spread over a clean surface of water. A tiny drop of, for example, oleic acid or benzene flashes over the surface as a film which drives floating particles before it. When a substance such as benzene or octane is poured over a clean surface of limited area so as to form a layer about a millimeter in depth and the air space over the water covered in so that it may become saturated with the vapor, the continuous sheet will be seen to break in places leaving open spaces which increase in size and fuse, until, in a brief while, there is left a lens of benzene or octane surrounded by a surface of water covered by a film of insensible thickness. There is, therefore, a natural plane of cleavage in a fluid spread on water, which is at an insensible but finite distance from the surface of the water.

The film left on the surface of the water when the excess has gathered into a lens I will call the primary film; and the surface itself a composite surface since its physical properties are neither those of a surface of benzene nor of water. A primary film may be defined in various ways: its vapor pressure obviously is equal to that of the surface of the lens and, as the curvature of this is slight, it is sensibly that of the vapor saturated at the particular temperature; the tension of the composite surface which it covers is sensibly equal to that of the sum of the surface tension of the pure substance (*e.g.*, benzene) and of the interface between it and water; finally the surface of natural cleavage mentioned above which encloses the primary film is placed where the attraction of the fluid for itself is equal to its attraction for the water on which it lies.

Spreading also sometimes occurs over the clean face of a solid to form a primary film in equilibrium with a lens and saturated vapor, and this gives yet another definition of a primary film, namely, that it is the film which gives the lowest value for static friction attainable without special treatment (see later on polishing) with that particular lubricant, on that particular solid.

The only layer of a fluid lubricant which can maintain itself against a normal pressure (it being always understood that the lubricant is a single pure chemical individual) is equal in thickness to two primary films, one belonging to each solid face. The only proof which need be adduced here is that when the slider has a curved face, the static friction is the same when the surfaces are flooded with the lubricant as it is when they are covered only by an invisible primary film formed by spreading from a drop or by condensation from the saturated vapor of the lubricant. When the surfaces are flooded, the excess lubricant is squeezed out until the two primary films alone remain; *the static friction is therefore independent of how the lubricant is applied and of the quantity present provided there is sufficient to form a primary film over each face.* The friction here referred to is however the steady value attained after the solid faces and the lubricant have come into equilibrium when the "latent period" of changing values has come to an end (see below).

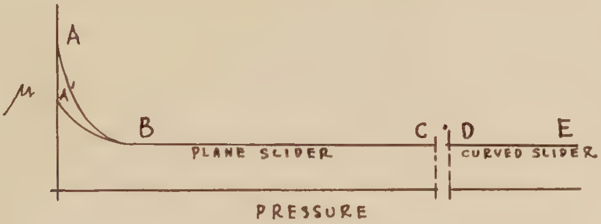

Fig. 1.

It should be noticed that the method of spreading over a solid is different from what it is over water. In the latter case a drop expands over the surface, in the former the drop seems unable directly to expand and the primary film is formed from its vapor. Chemical individuals with no sensible vapor pressure have been found not to spread over a solid face.[9]

The primary film is the seat of those boundary conditions in lubrication referred to by Osborn Reynolds, and characteristic of "dry" or "greasy" faces. It is interesting to enquire whether they are limited to that layer.

Experiments with a slider whose bearing surface is plane, prove that they are not so limited. Figure 1 shows a curve, not to scale, of μ plotted against the pressure—that is the load divided by the area of the bearing face. The portion *ABC* refers to a plane slider; the portions *D* and *E*, to a slider with curved face; and the scale of pressure is supposed to be broken between *C* and *D*, in order to bring the relatively enormous pressure under a curved slider on the paper.

Over *AB*, Amontons' law does not hold. Over *DE* it holds rigidly so far as the most exacting measurements show. There are therefore two states or stages in boundary lubrication, and the mechanism whereby the friction is adjusted to the load, is different in the two. In the first, which holds over *AB*, the layer of lubricant is maintained in place by those ordinary capillary forces which cause fluids to rise between two solid plates. Here the layer is many molecules thick, and the steady state is one in which capillary pressure balances the load. As the layer thins under increasing load, the friction rises, but not so fast as the load. Therefore the coefficient μ (= friction ÷ load) falls.

In the region *BCDE*, a layer of lubricant of great mechanical stability has been reached. Friction is no longer adjusted to the load by squeezing out lubricant, but by the elastic force between atoms.

When the load is varied, there is always a lag or latent period along *AB*, before a steady state is reached, which may amount to hours and in which the friction rises if the load has been increased and falls if it has been decreased. There is often a latent period in the region *BCDE*, but the lag is then due solely to variation in the degree of orientation of the molecules (see later).

Stanton [16] has proved by experiment that lubrication is still complete when the layer of oil is no more than 1.18 μ in thickness. Such a layer would however be about a thousand molecules deep, and, therefore, give ample scope for the variation in thickness mentioned above.

The following results were obtained by a slider with a spherical face resting on a plane surface, and enclosed in a chamber which was flooded with air carefully freed from all vapors.

Amontons' law was found to hold rigorously for a fifty-fold increase of load. The coefficient of friction μ was independent of the radius of curvature of the slider, of the load, and therefore of the area of contact. It was also independent of the temperature over the range investigated, namely, 15° C. to 110° C. Certain peculiar temperature effects at or about the melting points of solid lubricants, though of interest in themselves, need not delay us here as their theoretical importance is slight.[9]

The value of the coefficient of friction was found to be a function of only two variables, the nature of the solid faces, and the chemical nature of the lubricant. Within the same chemical series it was found to be a linear function of molecular weight. Putting on one side certain experimental complications, the solid state of the lubricant had no special significance; that is to say there was no break in the curve relating μ to molecular weight when, with increase in the latter, the members of a chemical series became solids.

In chain compounds and the simple ring series, benzene, naphthalene, anthracene, μ decreases as molecular weight increases and, as the relation is linear, the curve would if prolonged cut the base line of no static friction. Where it has been possible to test this expectation, it has been fulfilled,[5] that is to say the smallest force which it was possible to apply produced slipping.

It was possible with the apparatus used to apply a fluid lubricant to the clean faces in any one of three ways, namely, by placing the slider in a pool, by allowing a primary film to spread over the surfaces from a drop placed near one edge of the plate, or by passing the vapor of the lubricant into the chamber.

The last two methods were available only for those substances with a sensible vapor pressure, since, as has already been noticed, a drop does not expand over a solid face as it can over a fluid face, but spreads by condensation of its vapor.[6] The coefficient of friction was always found to be independent of the method of application, provided the air space was saturated with the vapor.

Solid lubricants were smeared on the faces or deposited from dilute solutions in ether. Microscopical examination of the surfaces showed that the superficial layers of even a solid lubricant fracture under the weight of the slider so that only a primary film remains; therefore, save when a hard crystallized layer was formed, the value of μ was normal in that it fell on an extension of the curve for fluid members of the series. It may be concluded, therefore, that there is a plane of cleavage enclosing a primary film in solids as well as in liquids when applied to a solid face.

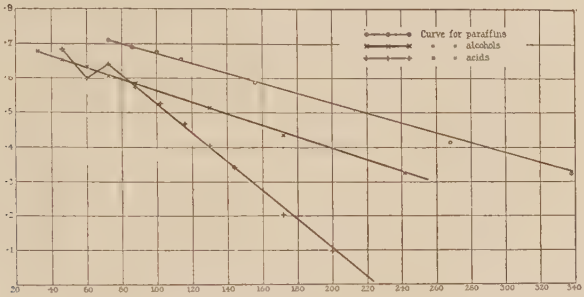

Fig. 2.—The three curves for glass. Ordinates, coefficient of static friction. Abscissæ, molecular weight.

Normal paraffins, acids and alcohols.—The values of μ for these substances on glass, steel or bismuth are given in Table I (Figures 2 and 3).

The figures for glass surfaces are plotted against molecular weight in Fig. 2, and the figures for the paraffins alone on surfaces of glass, steel and bismuth in Fig. 3. The curve in every case is a straight line and the effect of changing from one solid to another is merely to shift the line parallel to itself. The equation, therefore, is

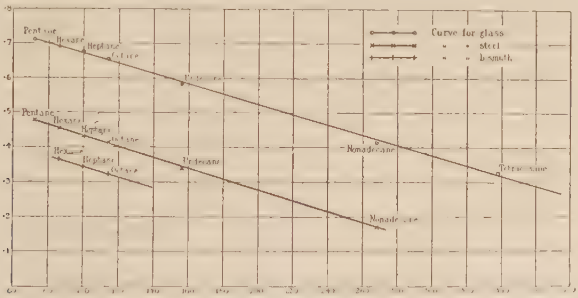

Fig. 3.—n-Paraffins.

$$\mu = b - aM \tag{1}$$

where M is molecular weight and a and b are parameters. The parameter a is independent of the nature of the solid faces and a pure function of the chemical type of the lubricant. The parameter b is dependent both upon the nature of the solid faces and upon the chemical type of the lubricant.

The influence of the nature of the solid faces appears decisively when these are of different material. When, for example, the slider is of glass and the plate of steel, the coefficient of friction is the exact mean of glass on glass and steel on steel for the particular lubricant. Taking octyl alcohol as an example μ for glass on glass is 0.5176, for steel on steel 0.2981 and the mean is 0.4078. Glass on steel gives $\mu = 0.41$. The agreement is closer in other cases. With amyl alcohol the mean is 0.48 and glass on steel gave 0.48. With octyl alcohol the figure for bismuth on steel is 0.270 and the mean is 0.274.

TABLE I

Lubricant	Glass	Steel	Bismuth
n-pentane	0.7102	0.4763	—
n-hexane	0.6908	0.4528	0.37
n-heptane	0.6751	0.4307	0.346
Iso-heptane	0.6683	—	—
n-octane	0.6552	0.4112	0.32
Undecane	0.5903	0.3421	—
Nonadecane (deposited from ether)	0.4119	0.1785	—
Tetracosane (deposited from ether)	0.3251	—	—
Methyl alcohol	0.6772	0.4610	0.29
Ethyl "	0.6512	0.4408	0.32
Propyl "	0.6301	0.4173	0.34
Butyl "	0.6061	0.3924	0.30
Iso-butyl "	0.6273	—	—
Amyl "	0.5854	0.3752	0.27
Octyl "	0.5176	0.2981	0.25
Caprylic "	0.5373	—	—
Undecylic "	0.4455	0.2298	—
Cetyl "	0.3253	0.1143	0.17
Formic acid	0.6823	—	0.45
Acetic "	0.6003	—	0.40
Propionic acid	0.6387	—	3.31
Butyric "	0.5721	—	—
Valeranic "	0.5259	—	0.28
Hexoic "	0.4654	0.3108	—
Heptoic "	0.4051	0.2556	—
Caprylic "	0.3417	0.2003	0.19
Decoic "	0.2006	0.0741	—
Dodecoic "	0.0983	—	—
Myristic "	Unmeasurable; slider moves with the weight of the scale pan = 0.7 gr.		
Palmitic "			
Stearic "			

These results show that, wherever the plane of slip may be placed, the attraction field of the solids is in some way conducted to it, unless indeed slipping is confined to the two interfaces between lubricant and solid. It is not likely to be there because the field of the solid will be strongest and cohesion greatest in those planes.

The answer to the question why lengthening the chain of carbon atoms should diminish friction is not in my opinion forthcoming. The nature of the difficulty is made obvious by considering an analogous case. When a chlorine atom is introduced at one end of the molecule of a primary acid, the attraction for the hydrogen atom of the carboxyl group at the other end is weakened and the dissociation constant of the acid thereby raised. This effect decreases in proportion to the number of carbon atoms in the chain so that, if we conceive of the chlorine atom repelling the hydrogen atom, then each carbon atom absorbs so to speak a constant fraction of the total repulsion.*

Guided by this analogy we must seek for some influence exerted by the solids which can be transmitted to the plane of slip but in such a way that the effect diminishes with the number of carbon atoms in the transmitting chain. It cannot be a repulsion, because lengthening the carbon chain would then increase friction. It must be an attraction, in which case the friction will be that due to the CH_3 groups which are in contact at the plane of slip together with the transmitted attraction of the solids. But when the chain of carbon atoms has been lengthened sufficiently to eliminate the attraction of the solids, that of the CH_3 groups would still remain and the friction would not vanish as experiment shows it does vanish. The hypothesis in this form would, therefore, seem to be valid only if the terminal CH_3 groups of the paraffin chain have no attraction for each other.

Equation (1) is indeed remarkable in that the molecules of the lubricant make no positive contribution to the friction. They seem merely to shield or "saturate," in the chemical sense, the attraction fields of the solids.

Possibly an answer is to be found in the increase in lateral cohesion of the long molecules with increase in the length of the carbon chain. This would give greater mechanical stability to the layer of lubricant.

The simple linear relation is not disturbed when more complicated molecules are concerned, so long as the carbon chain is continuous. The coefficients of friction on glass and steel of the optically active carbinols of the formula $C_2H_5 . CH(OH) . C_nH_{2n+1}$ have been measured by Miss Doubleday and they conform to the equation $\mu = a - bM$. It appears also in the ring series benzene, naphthalene and anthracene.

Other Substances.—A preliminary survey of the relation of lubrication to chemical constitution, in which nearly one hundred substances were examined, shows relations which cannot at present be focused by any simple theory. It should be noted that the measurements were undertaken before the necessity for extreme chemical purity was grasped. Some of the values are given in Table II.

TABLE II

STATIC FRICTION FOR CLEAN FACES OF BISMUTH

CHAIN COMPOUNDS

ALCOHOLS

	Static Friction		Static Friction
Methyl	.29	Isopropyl	.32
Ethyl	.32	Isobutyl	.30
Propyl	.34	Allyl	.29
Butyl	.30	Glycol	.30
Amyl	.27	Glycerol	.22
Octyl	.25	Penterythritol	.40
Cetyl	.17		

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* See paper by I. Langmuir, this volume. J. A.

ACIDS

	Static Friction
Formic	.45
Acetic	.40
Propionic	.31
Valeric	.28
Carpryllic, fluid	.19
“ frozen on plate	.05
Acetone	.32
Methyl ethyl ketone	.29
Ethyl acetate	.36
“ valerianate	.35
Tristearin	.24
Triolein	.14
Acetone di carboxylic di ethyl ester	.29
n. Hexane	.37
n. Heptane	.346
n. Octane	.32

	Static Friction
Stearic	.15
Oleic	.10
Ricinolic	.02
α Lactic	.20
Glyceric	.22
B.P. “Paraffin”	.20
Solid paraffin, m.p. 30.5	.09
“ “ m.p. 46	.07
Carbon tetrachloride	.43
Chloroform	.30
Amylene	.26
Octylene	.28
Ethyl ether	.33
Butyl xylene	.27

Ring Compounds

Benzene	.34
Ethyl benzene	.32
Iodo benzene	.30
Toluene	.28
Xylene	.30
p-Cymeme	.31
Phenol	.25
Catechol	.39
Quinol	.40
m-Cresol	.26
Benzyl alcohol	.31
Pyridine	.33
Piperidine	.32
Naphthalene	.29
Anthracene	.26
β Naphthol	.38
Naphthoic acid	.39

Benzoic acid	.38
Phthalic acid	.37
Cinnamic acid	.27
Benzilic acid	.45
Salicylic acid	.41
Ethyl benzoate	.33
o-Phthalic ester	.27
Ethyl hydrocinnamate	.28
Ethyl cinnamate	.32
Thiophenol	.22
Benzylhydrosulphide	.23
Carvacrol	.23
Thymol	.24
Menthol	.26
di Pentene	.31
Camphor	.24
Active ethyl ester of Camphor oxime	.33
Iso-Cholesterol	.27

Cyclic Compounds

Cyclohexane	.31
Methyl cyclohexane	.30
1.3 di Methyl cyclohexane	.29
Cyclohexanol	.20
1.2. Methyl Cyclohexanol	.28
1.3. “ “	.35
Ammonia fortiss	.34
Triethylamine	.30
Tripropylamine	.26

Cyclohexanone	.35
1.2. Methyl cyclohexanone	.32
1.3. “ “	.35
1.4. “ “	.33
Castor oil	.03
Water	.33

The relation of lubricating qualities to viscosity broadly resembles that to molecular weight. In a simple chemical series lubrication and viscosity change in much the same way with molecular weight; but that there is no fundamental relation between viscosity and lubrication is shown by the following figures:

	Viscosity at 20°	Static Friction
Carbon tetrachloride	.0096	.43
Chloroform	.0056	.30
Acetic acid	.0122	.40
Octyllic acid	.0575	.19
Benzene	.0065	.39
Toluene	.0058	.28
Benzyl alcohol	.0558	.31

The most interesting feature of Table II is the contrast between chain and ring compounds. Any change in molecular structure appears to have opposite effects according as it occurs in a ring or chain compound. Thus a double bond decreases the lubricating action of a ring compound, but increases that of a chain compound. As examples, compare naphthoic acid with double-bonded oxygen, with naphthalene; menthone with menthol; cyclohexanone with cyclohexane; benzoic acid with benzene. As examples of double-bonded carbon, compare cinnamic ester with hydro-cinnamic ester; di-pentene, having two unsaturated carbon atoms, with menthol and cyclohexane. Also the more saturated cyclic compounds are better lubricants than the less saturated ring compounds.

When a ring or chain are joined, as in butylxylene, the result is a better lubricant than either.

The esters occupy a quite unexpected position. The simple aliphatic esters are much worse lubricants than their related acids and alcohols. The ring esters, on the contrary, are better lubricants than are their related acids (*e.g.,* ethyl benzoate and benzoic acid).

Perhaps the most interesting substances are the hydroxy-acids with OH and COOH groups. This conjunction produces a remarkable increase in the lubricating power of a chain compound (lactic acid and ricinolic acid), and almost destroys lubricating action in the case of the ring compounds (salicylic and benzylic acids).

In the ring compounds the replacement of hydrogen decreases lubricating power in the case of N, : O, or . COOH, and increases it in the case of other groups in the order $C_2H_5 < CH_3 < OH$.

The effect of a second group of the same or of a different kind is to decrease the effect of the first. Compare, for instance, toluene with xylene; catechol quinol and cresol with phenol; and methyl cyclohexanol with cyclohexanol. The simpler the group the more effective it is. Compare cymene with toluene or xylene, and benzyl alcohol with phenol.

When the atoms are disposed with complete symmetry about a carbon atom, the result is a very bad lubricant, as we see in carbon tetrachloride and the alcohol penterythritol $C(CH_2OH)_4$.

It will be noticed that no ring compound is a good lubricant. Even cholesterol, with the molecular weight 366, is no exception.

The group SH acts much as OH, thiophenol C_6H_5SH and benzylhydrosulphide $C_6H_5 . CH_2SH$ resembling phenol and benzyl alcohol respectively.

Two Component Systems.—The limited number of cases which have been studied[9] in which two different chemical substances, each rigorously pure, are present on the surfaces fall into two sharply distinct classes according to whether the substances are or are not miscible. In both cases it will be wiser to give the facts, which are straightforward, before attempting an explanation.

(a) *The Two Substances are Miscible.*—The effect of varying the proportion of two constituents in a mixture was found to depend upon the relative lubricating properties of the individuals, and upon the chemical constitution of the substances. The three types of curves found are illustrated in Figure 4. They are (1) mixtures of aliphatic acids or alcohols with paraffins, *e.g.*, caprylic acid with undecane. The coefficient of friction is that of the pure acid or alcohol until the quantity present in the mixture falls to about 0.7 per cent. The acid or alcohol is adsorbed by the solid surface to form a primary film composed wholly of its molecules until the percentage falls to 0.7 per cent, when the paraffin molecules begin to find a place in the film.

(2) Mixtures of aliphatic acids and alcohols and of lactic acid with water. The primary film throughout seems to contain both kinds of molecules, but those of the better lubricant are in excess until a critical point is reached, when the change in the direction of the curve indicates an increased invasion of the film by the molecules of the worse lubricant.

(3) Mixtures of aliphatic acids and alcohols which do not greatly differ in their lubricating properties. The curve is a straight line joining the extremes; that is to say the effect of each constituent is proportional to its relative mass (*e.g.*, hexoic acid and octyl alcohol).

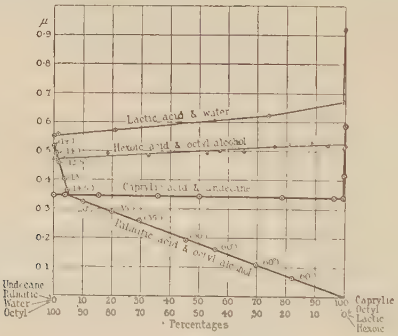

Fig. 4.—Percentages.

The curves are isomers except that for palmitic acid and octyl alcohol. The miscibility of this pair is so low as to make it necessary to raise the temperature as the percentage of acid is increased. The figure in brackets gives the temperature at which a measurement was made. It will be noticed that there are no breaks in the curves corresponding to the changes of temperature.

In general the curves show that the better lubricant of a pair is more strongly adsorbed by the solid face, but they equally prove that this is not the only factor operating.

(b) *The Two Substances are Immiscible.*—Of this class pairs of which either water or benzene was one have alone been studied.

Water considered as a lubricant is of a remarkable character. On clean faces of glass, quartz, or steel, it is a "neutral" substance—that is to say it does not alter the friction. Its molecular weight is of course low and, therefore, the effect likely to be small, but a molecular weight of 18 on the curve for either paraffins or alcohols would give a value of μ decisively different from that for a "clean" face. Be this as it may, it can certainly be said that the most careful measurements failed to reveal any fall in friction due to the presence of water.

Water also has a profoundly disturbing effect upon the lubricating properties of other substances. Its vapor will, for instance, almost wholly destroy the lubricating properties of an alcohol.

On the other hand water can be an excellent lubricant. It is such for ebonite, or for glass or steel when already covered with a film of a solid lubricant which does not dissolve in water.

These apparently contrary properties were found to be reconcilable when the influence of water was followed in a number of cases.

When water vapor is admitted to the chamber its influence on the friction of clean surfaces of glass, quartz or steel is nil, but if the surfaces have already been lubricated by a primary film, water vapor *lowers friction if the lubricant is immiscible with water and raises friction if the contrary is the case.* No exception to this simple rule was found.

Up to a certain point the mode of action of the vapor is clear. Consider, as the simplest case, a surface covered with a primary film of a solid paraffin. Water vapor diminishes the friction of the surface of a block of solid paraffin —the vapor condenses as an insensible primary film of water which has considerable lubricating power as the following figures show:

Paraffin on paraffin ($C_{24}H_{50}$) in dry air $\mu = 0.076$
water vapor admitted $\mu = 0.019$

When therefore surfaces of glass or steel are coated with a layer of paraffin, water will reduce their friction even though the layer of paraffin be only a film of insensible thickness.

We must, therefore, suppose that when water vapor condenses on to a primary film of paraffin on a solid, the value of μ is that given by *four* primary films, two median ones of water, two outer ones of paraffin, one on each solid face, and the conclusion reached is that four films lubricate better than two. This may be of the nature of a general law.

The doubled films can be disturbed by moving the slider about over the surface, when the friction at once rises.

A similar double primary film can be deposited readily even when the first lubricant applied is a liquid provided it be immiscible with water. This would be remarkable had we not convincing evidence that a primary film on a solid is always itself a solid. Such films, as might be expected, are easily broken up by moving the slider about on the plate when the friction at once rises nearly to the "clean" value.

The action of water seems paradoxical in that when the doubled films are broken up by mechanical agitation such as is produced by moving the slider backwards and forwards over the surface, or without mechanical agitation by the vapor of water when admitted to surfaces covered by a primary film of a lubricant miscible with water, the bad lubricant, water, seems capable of displacing any good lubricant. It would appear, therefore, that in this case the worse lubricant is more strongly adsorbed by the solid face.

When the surfaces have been lubricated by a lubricant miscible with water, such as, *e.g.*, the lower aliphatic acids, or the alcohols, the effect of water vapor always is to raise friction.

Benzene vapor, unlike water vapor, always slightly lowers the friction of surfaces already lubricated by primary films of substances miscible with it.

The Latent Period.—When the normal paraffins and their related normal acids and alcohols are studied as lubricants, a singular fact emerges. Over the region *BCDE* in Figure 1 the friction of solid faces lubricated with one of these acids or alcohols takes from five minutes to an hour or more to come to a steady state.

Immediately after the lubricant is applied, the friction is high, and throughout the "latent period" it falls until the final steady value is reached. Now the molecules of these substances are highly polar, being chains of carbon atoms loaded at one end with the $-COOH$, or $-CH_2OH$ group. The attraction of the two ends of the molecule for the solid face is certain to differ greatly, and the latent period may be supposed to be the time occupied in reaching the maximal degree of orientation of the molecules of the lubricant at the face.

If this supposition be correct, lubricants composed of molecules whose ends are alike should show no latent period. Such are the normal paraffins, and, actually, surfaces lubricated with one of these do not under any circumstances exhibit the remarkable delay in reaching a steady state. The first observed value of friction is the same as the last.

What is the final "steady" state? Is it one in which all the molecules are oriented, so that the loaded ends are directed towards the nearest solid face? The study of friction shows that it is not.

When a pool of lubricant is placed on a solid face, or when a clean solid face is immersed in the vapor of the lubricant, some of the molecules will be presented right and others wrong end to the solid. During the latent period the wrongly oriented molecules are being replaced with rightly ended ones by the process of evaporation into and condensation from the overlying fluid or vapor. The process will not continue until all the molecules are rightly oriented, because evaporation and condensation does not cease, and some of the molecules arriving at the face will reach there wrong end first. The steady state is, in fact, an average state determined by the difference between the attraction of the solid for the two ends of the molecules.

The friction of surfaces in equilibrium with either the vapor or fluid lubricant is, however, not the lowest which the particular acid or alcohol can give. This is reached only after the slider has been on the plate for some time. Enclosing the layer of lubricant between two solid faces increases the degree of orientation, as might be expected, since the excess fluid or vapor is squeezed out and the process of condensation and evaporation thereby arrested. Readjustment of wrongly oriented molecules goes on in these enclosed layers until what may possibly be complete orientation is reached.

An example will perhaps assist in making this clear.

Lubricant: Caprylic acid on glass. (1) A pool of the lubricant placed on the plate, the curved slider at once put into it, and readings at once taken. This is the initial state, in which the degree of orientation is at its lowest. The coefficient of friction $\mu = 0.57$, and the time taken to fall to the final steady value when $\mu = 0.34$, the surfaces being kept as quiet as possible, was 60 minutes.

(2) The slider and plate were exposed in a chamber to the saturated vapor of the acid for three hours. The former was then placed on the latter, of course without opening the chamber, and a reading taken as quickly as possible. This gives an approximation to the friction of faces in equilibrium with vapor. The initial reading gave $\mu = 0.45$, which fell to the steady value $\mu = 0.34$ in about five minutes.

(3) To get the friction of surfaces in equilibrium with *fluid* lubricant, both surfaces were covered with an excess of the acid and, three hours later, were

placed in contact, when μ was found to be 0.39, which fell in about ten minutes to the value 0.34.

Here there is sufficient evidence for the existence of different degrees of orientation in the layer of lubricant condensed on to the solid face according as it is in equilibrium with fluid, or vapor, or enclosed between two solid faces.

For more than ten years I have urged that orientation of molecules at an interface must spread into the overlying fluid until it is destroyed by the heat motions. The "capillary" layer in other words is not one but, it may be, many molecules deep and its depth is a function of the degree of polarity of the molecules and of temperature. The study of the latent period seems to afford valuable evidence in support of this view.

How might orientation in a liquid be expected to reveal itself? When a lubricant is very viscous it takes an appreciable time to squeeze out the excess fluid from between the slider and plate. Glycerol is such a lubricant, and the first recorded values of friction are always small, but they rise slowly until they reach the value for clean unlubricated surfaces of glass. Glycerol, in fact, like water, is neutral to glass in that it does not, in the strict sense, lower the friction of its surface. Glycerol, like water, can of course provide a buffer of fluid and so act as a lubricant in the hydrodynamic sense of Osborne Reynolds' theory. It is not a lubricant in boundary lubrication, though owing to viscosity, the fact needs some patience for its detection. When water, which has a low viscosity, is used, the full "clean" value of friction was always got at once.

High viscosity therefore tends to give an initial abnormally low value of friction, which rises more or less rapidly as the buffering layer of fluid is squeezed out.

Any degree of orientation of the molecules of a fluid might be expected to increase its viscosity, since the average random disposition upon which the normal viscosity depends is departed from. If the rise in viscosity were sufficient it could be detected by an initial abnormally *low* value of friction. This expectation is realized with aliphatic acids and alcohols. When the surfaces are allowed to come into equilibrium with *fluid* lubricant before being put in contact, as in (3) above, the first readings are always abnormally low. For example, and still keeping to the case of caprylic acid, the first reading, taken as quickly as possible, gave $\mu = 0.26$ and the friction then rose rapidly to $\mu = 0.39$—too rapidly to permit of the time being recorded.

The effect of mechanical agitation is surprising. Moving the slider backwards and forwards on the plate will, for example, shorten the latent period of caprylic acid [case (1) above] from 60 minutes to 10 minutes. The temperature coefficient of the latent period is high, *e.g.*:

HEPTOIC ACID ON GLASS

Temperature	Latent Period in Minutes
15° C.	45
48° C.	15
72° C.	5

The value of μ in the final state is independent of temperature within the limits of accuracy of the method (down to the third place of decimals) over the range tried, namely, from 13° C. to 110° C.[8]

Incomplete Primary Films.—These have been studied for one substance, namely ethyl alcohol. Since the complete film is defined by having the pressure of saturated vapor, incomplete films can be formed by exposing the solid surfaces to a lower vapor pressure. The results are plotted in Fig. 5. Over the greater part of the curves the coefficient of friction is a linear function of the vapor pressure and the effect of a change in the nature of the solid face again is to shift the curves parallel to themselves. The equation, therefore, save where the vapor pressure is very low, is $\mu = \alpha - \beta P$ where P is the vapor pressure.

The Structure of a Primary Film.—The work of Langmuir and Adam proves that in a primary film composed of chain compounds, the chains of carbon atoms are disposed at right angles to the surface throughout the film or at any rate in the layer of molecules attached to a face of water. These writers, following Devaux, claim that a fully formed primary film is composed of a single layer of molecules—it is the monomolecular film of which so much has been written—but, though a primary film composed of a substance possessed of no sensible vapor pressure may be monomolecular, all primary films are not so constituted. It must be remembered here that a primary film is defined by a certain plane of natural cleavage and that its vapor pressure is equal to that of saturated vapor.

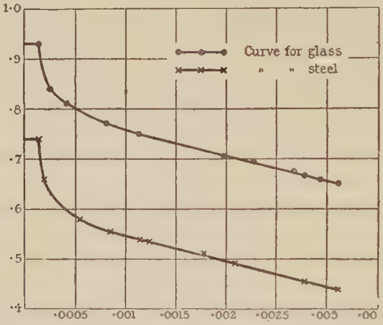

FIG. 5.—Abscissæ, number of gram-molecules of Cl_2H_5OH per litre of air. Ordinates, coefficient of static friction.

Consider a primary film of say octyl alcohol in equilibrium with saturated vapor and a flat lens resting, with the film, on water or a solid. This condition is readily realized. The work needed to detach a molecule of the alcohol from the primary film must be such that the number leaving the film in unit time to be set free in the vapor must, on the average, be equal to those passing from the vapor to the film. There is no reason why a monomolecular film should be peculiarly fitted to comply with this condition, indeed, it is probable that it rarely does so.

Complete, that is fluid, lubrication has been frequently mentioned in the previous pages. The theory was first worked out by Osborne Reynolds on the basis of certain novel experiments made by Tower with cylindrical bearings so constructed as to maintain an excess of fluid between the solid surfaces. Reynolds' treatment has been simplified by Sommerfeld and Rayleigh. It may be useful to those unfamiliar with the theory, to present it in the briefest outline in the form given by Rayleigh.[14]

It starts with the assumption that, if the layer of oil which is maintained between the surfaces by the dragging action of the surfaces themselves, is thick enough to eliminate the "unknown boundary actions," as Reynolds calls them, the results of the experiment should be capable of derivation from the ordinary equations of hydrodynamics. The assumption reduces the friction to the simple internal friction of a viscous fluid.

Consider two plane surfaces with fluid between, and let one surface be of unlimited extent, whilst the other is of unlimited extent along z, but is limited at $x = a$, and at $x = b$. Let the two surfaces approach without tangential motion, the fluid then has to be squeezed out and the tangential velocity will be nothing at the middle of the surface, namely, at $x = \frac{1}{2}(a - b)$, and greatest at the ends. The motion will be resisted by the internal friction of the fluid, and as this is proportional to the velocity and equal and opposite to the pressure, the pressure is greatest at the middle and vanishes at the edges. If there be tangential motion of velocity U of one of the planes, the fluid will be dragged along with it, and there will be a gradient of velocity in the fluid from U at the moving plane to 0 at the stationary plane, the internal friction again being opposed by a pressure.

Let the two parallel planes be at $y = 0$ and $y = h$, and let the motion be everywhere parallel to x, so that the velocity components v and w are everywhere zero, an element of volume (dx, dy) is subject to the force $\eta(d^2\mu/dy^2)\,dx\,dy$, where η is the coefficient of internal friction. Since there is no acceleration this force is balanced by that due to the pressure, namely $-(dp/dx)\,dx\,dy$, and thus—

$$\frac{dp}{dx} = \eta\frac{d^2\mu}{dy^2} \qquad (1)$$

On integrating, having regard to the fact that at $y = 0$, $u = -U$; and at $y = h$, $u = 0$, we get—

$$u = \frac{y^2 - hy}{2\eta}\cdot\frac{dp}{dx} - \left(1 - \frac{y}{h}\right)U \qquad (2)$$

The whole flow of the fluid between the surfaces is—

$$\int_0^h u\,dy = -\frac{h^3}{12\eta}\,\frac{dp}{dx} - \frac{hU}{2} = -Q$$

where Q is constant, so that—

$$\frac{dp}{dx} = -\frac{6\eta U}{h^3}\left(h - \frac{2Q}{U}\right) \qquad (3)$$

or, putting $H = 2Q/U$—

$$\frac{dp}{dx} = -\frac{d\eta U}{h^3}(h - H) \qquad (4)$$

The assumption so far is that the whole motion is unidimensional, but (4) is approximately applicable if h is variable, and always small, provided that the variations are not too abrupt.

The total pressure or load P is—

$$P = \int_a^b p\,dx = -\int_a^b x\,\frac{dp}{dx}\,dx$$

on integrating by parts—the integrated term vanishing because $p = 0$ at the ends.

Hence by (4)—

$$\frac{P}{6\eta U} = \int_a^b \frac{x\,dx}{h^2} - H\int_a^b \frac{x\,dx}{h^3} \qquad (5)$$

The tangential traction exerted by the liquid on the moving plane is got from (2) and (4) by putting $y = 0$ when—

$$f = \eta \frac{du}{dy} = \eta U \frac{4h - 3H}{h^2} \qquad (6)$$

The total friction F is therefore—

$$\frac{F}{\eta U} = 4 \int_a^b \frac{dx}{h} - 3H \int_a^b \frac{dx}{h^2} \qquad (7)$$

Comparing (5) and (7) we see that the ratio of the total friction to the total load ($F/P = \mu$) is independent of η and of U, and, since the right-hand members of (5) and (7) are dimensionless, it is independent of the linear scale. We thus arrive at Amontons' law from purely hydrodynamical considerations, the friction being independent of the area, provided the distance between the surfaces (h) is altered in the same proportion as the length.

In the simple case, when both surfaces are plane and one is inclined at a very small angle to the other, so that h has the values h_1 at $x = a$, and h_2 at $x = b$, it can be shown that the load varies as the second power, and the total friction as the first power of the length divided by the distance h_1.

The pressure (p) will always adjust itself to the load (P) by alteration in the distances between the surfaces (h), for the nearer the surfaces the greater would be the friction and consequent pressure for the same velocity, so that the surfaces would approach until the pressure balanced the load.

Let us suppose the faces forced closer together by increased pressure. The hydrodynamical equation will continue to hold so long as the fundamental assumption is complied with, namely, that of fluidity of the lubricant. According to this the motion will be distributed throughout the whole region from $y = 0$ to $y = h$. So long, however, as the condition of fluidity is fulfilled there will be no static friction.

An obvious assumption is that the layer of lubricant immediately in contact with the solid faces is fixed in position and that static friction comes in only when these layers get into contact. On this assumption the length h, over which fluidity is supposed to be complete, does not correspond with the distance between the original solid faces. This assumption is at one with the usual assumptions made in calculations concerning the flow of fluid past solid boundaries.

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The Mechanism of Coagulation

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Introduction

The essential difference between a true solution and a colloidal system is to be sought in the fact that, though both are dispersed systems, the former is a stable and the latter an unstable system. When we have sugar dissolved in water, the homogeneous solution has less free energy than the separate solid and liquid phases. When we have gold dispersed in water the sol has an excess of free energy compared with the separate phases. As there is no reciprocal action (or at least hardly any) between the two components in the latter case, the fine division is the cause of this excess of energy, viz., as free surface energy. As the free energy tends to a minimum, the surface energy tries to lessen the surface of the dispersed particles, to attach these particles one to another, to *coagulate* the colloidal "solution."

Coagulation therefore is the grouping together of the dispersed particles; the ordinarily accompanying fact of precipitation of the coagulum is only a secondary phenomenon, consequent upon the fact that, according to Stokes' law, larger particles sink more rapidly than smaller ones. But, as Perrin[1] has pointed out, a certain distribution of the particles always takes place (even in true solutions); therefore a settling out of coarse colloidal particles in such a way that a mere stirring is sufficient to restore the sol in the same degree of dispersion, has nothing to do with (reversible) coagulation.

As the coagulated system is more stable than the sol, the question arises why the colloidal system can exist at all. Why does the free surface energy not cause an immediate coalescence of the particles? Let us consider what is necessary for this to occur. In order that two particles coalesce it is necessary first of all that the particles collide. Of course the Brownian movement can cause this and the calculus of probabilities can estimate the chances of collision with particles of given size, in a given liquid, at a given temperature, when the mean distance of the particles is known. The *probability of collision* therefore is the first factor dominating the problem of coagulation. But it is not the only one, for the second question which arises is whether every collision really effects a coalescence of the particles brought together by the Brownian movement. As the probability of collision of an ordinary sol is very great, there must be some reason why the probability of the coalescence of the two meeting particles in a "stable" sol is rather small. Thus the *probability of adhesion, i.e.,* the ratio of the number of collisions that lead to a union to the total number of probable collisions, is the second factor to be considered in a discussion of the mechanism of coagulation.

The investigations on the stability of sols carried out during the last 25 years, especially since those of Hardy,[2] showed that the electrical charge of the particles is an important factor in preventing their union, coagulation taking place when the charge is removed (at least partly, according to Powis[3]). The electric charge rules the probability of adherence, not that of collision, though this is often erroneously thought to be the case. Svedberg[4] pointed out that an electrolyte, though affecting the charge of the particles, does not alter their Brownian movement, as long as no adhesion of the particles sets in. Quite the same may be said concerning the so-called "protective action" of substances like gelatin; they affect only the probability of adhesion, at least when their concentration is too small to alter the viscosity of the system, which would influence the Brownian movement according to Stokes' law. A protective action can be exercised, however, by other substances than purposely added protective colloids; water molecules adhering to the particles and so forming an aqueous envelope around each of them, can exercise a considerable influence on the probability of adhesion, as will be seen later. This is especially the case with lyophilic colloids (emulsoids). (See further on.)

We shall discuss first that part of coagulation which is ruled by the probability of collision. For this purpose we must consider a sol deprived of all stabilizing factors, so that every collision causes a union of the colliding particles (probability of adhesion = 1).

2. Coagulation of an Uncharged Suspensoid

Von Smoluchowski[5] has developed a theory for the mechanism and the velocity of this process and several other investigators controlled it and found it to be correct for the case we are discussing now.*

We have just pointed out that uncharged particles must attract each other in consequence of their surface tension; according to Von Smoluchowski there must be a sphere of attraction around every particle of such a nature that any other particle whose center enters this sphere will be firmly retained. R is the radius of this sphere of attraction, and R must be at least $2r$, when r is the radius of the particle itself.

Now Von Smoluchowski discusses this problem: what is the probability w that one particle (which we shall consider as motionless) in a sol, containing ν_0 particles per cc., gets another particle within its sphere of attraction? The formula expressing this is

$$w = 4\pi DR$$

when D is the mean displacement of a particle in consequence of the Brownian movement, *i.e.*,

$$D = \frac{R'T'}{N}\frac{1}{6\pi\eta r}, \qquad (1)$$

R' being the constant of the gas law, N the Avogadro number, T' the absolute temperature (in degrees Kelvin), η the viscosity. Thus starting from ν_0 single particles, there will be ν_1 of them after a time t so that

$$\nu_1 = \nu_0 e^{-4\pi DR\nu_0 t}$$

Their decrease is therefore

$$-\frac{d\nu_1}{\nu_1} = 4\pi DR\nu_0\vartheta t.$$

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* A very remarkable deduction of the equations, to which von Smoluchowski's theory led, is to be found in a recent paper of Jablczynski.[13]

When only a small part have come together we can take $\nu_0 = \nu_1$ and integrating this last equation, we get

$$\nu_1 = \frac{\nu_0}{1 + 4\pi D R \nu_0 t} = \frac{\nu_0}{1 + \frac{t}{T}}$$

where T, the so-called *time of coagulation,* is $T = \frac{1}{4\pi D R \nu_0}$ or for reasons of abbreviation $T = \frac{1}{\alpha \nu_0}$. When we take the particle as moving itself too, we get:

$$\nu_1 = \frac{\nu_0}{1 + \frac{2t}{T}}.$$

There will not only be double particles, but these will meet with each other to form quadruple ones, or, if they meet other single particles, triple ones, etc. We can make a similar calculation for them if we knew their constants D and R. Now Von Smoluchowski makes the assumption, that, when D_i is the constant of displacement for a particle, consisting of i single ones, D_k that of one composed by k primary ones, and D_{ik} that of their combination, that $D_{ik} = D_i + D_k$ and in the same line of thoughts that $R_{ik} = \frac{1}{2}(R_i + R_k)$. This last simplification is indeed rather risky.

Thus Von Smoluchowski, taking in account the formation of complex particles ν_1, ν_2, ν_3, etc., found these numbers to be

$$\nu_1 = \frac{\nu_0}{1 + \left(\frac{t}{T}\right)^2} \quad \text{or} \quad \frac{\nu_0}{(1 + \alpha\nu_0 t)^2} \tag{2}$$

$$\nu_2 = \nu_0 \frac{\alpha \nu_0 t}{(1 + \alpha \nu_0 t)^3}$$

. . . .

$$\nu_k = \nu_0 \frac{(\alpha \nu_0 t)^{k-1}}{(1 + \alpha \nu_0 t)^{k+1}}$$

The total number of particles, *i.e.*, the sum of all single, double, triple ones, etc., is given by the equation

$$\Sigma\nu = \frac{\nu_0}{1 + \frac{t}{T}} \tag{3}$$

From this equation we understand, why T is called "time of coagulation"; for after a time T, when $t = T$, according to this equation the number of particles is just halved; T therefore is a good characteristic for the rate of coagulation.

In Fig. 1 a graphical representation is given how the total number of all particles $\Sigma\nu$, how the number of the single ones ν_1, the double ones ν_2, etc., vary with time. These numbers are the ordinates and they are expressed as parts of the original number ν_0. Time is measured with the "coagulation time" T as a unity (abscissæ). Originally there are of course only single particles, the curves for $\Sigma\nu$ and for ν_1 thus start from the same point. It is also a matter of course, that both these curves fall steadily; however, the number of double particles, originally O, rises at first, but as they will coalesce more and more with each other or with other particles, their curve will reach a maximum and then fall too. The same will be the case with the triple, the quadruple ones, etc., according to the equations given above, the maximum for the more complex particles always moving to a later moment in the process of coagulation.

Zsigmondy and his pupils[6] made splendid investigations to check *von Smoluchowski's* theory for gold sols and *Kruyt* and *van Arkel*[7] did the same kind of work for the sol of selenium. In all these researches an excellent agreement was found between theory and experiment in the case of "rapid" coagulation, *i.e.*, when the probability of adhesion was really 1 or approximately so (by adding electrolytes in a concentration sufficient to diminish the electric charge of these suspensoids to 0, or at least below the critical value, as will be discussed later on.

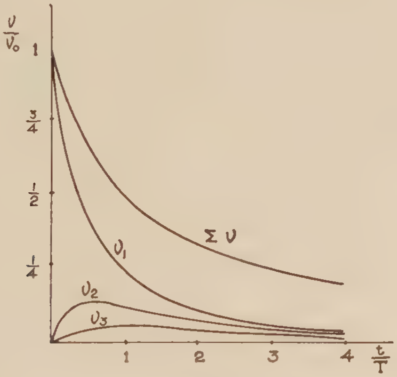

FIG. 1.

To see whether the mechanism of "rapid" coagulation really happens according to the outline given, the number of the single particles or the total number of all should be counted during the process of coagulation. With the gold sol it is possible to distinguish single particles from complex ones, as the former, when seen in the ultramicroscope, were green, the latter yellow. In this way equation (2) was successfully checked; but all other researches in the field aimed at the verification of equation (3) for Σv. Experiments were carried out in this way: by means of a screen with square opening a parallelopipedon of known dimensions is made the only visible part of the light cone of an ultramicroscope. Now a dilution is made of the sol to such an extent that there are generally 2 or 3 particles visible at the same time. By making 200 countings the mean number of particles is established, and thus the number of particles in 1 cc. of the original sol can be calculated. Then electrolyte solution can be added to a portion of the sol; coagulation sets in and can be stopped after a certain time by adding to the sol a protective colloid. Then again a dilution is made and the number of particles is counted; by repeating this process after the electrolyte has acted various times, a series of values for Σv is found.

As an example we give Table I according to an investigation of Westgren and Reitströtter.[8]

TABLE I

Gold sol, average diameter of particles: 96 μμ.
Coagulating agent: NaCl, 86 mmol. p. L.
Sol concentration: 5.22×10^8 particles p. c.c.

Time in Minutes	10^{-8} Number of Particles per C.C.	T in Min.	Calculated Number of Part. $\times 10^{-8}$ if $T = 5.3$ Min.
0	5.22	—	5.22
1	4.35	5.0	4.39
2	3.63	4.6	3.78
3	3.38	5.5	3.33
5	2.75	5.6	2.68
7	2.31	5.5	2.25

From this table we see that calculating according to eq. (3) we find a constant value for T, or taking the mean value, 5.3, for T, we find a fair agreement between observed and calculated numbers. The equation thus proves to give a good understanding for the phenomenon.

By means of equations (1) and (3) we can calculate $\frac{R}{r}$, the proportion between the diameter of the sphere of attraction and that of the particle. This calculation leads to the result that this value lies between 2 and 3. This result is also in harmony with the theory, and is discussed by von Smoluchowski and Zsigmondy in their papers mentioned above.

Several other consequences of this theory could be checked. From the equation $T = \frac{1}{4\pi D R \nu_0}$ can be seen easily how T changes with relation to the initial concentration of the sol; ν_0 is proportional to that concentration, so T must be proportional to the dilution. In good agreement *Kruyt* and *van Arkel*[7] found for a selenium sol diluted in the proportions 1:1, 1:2 and 1:10 respectively. $T = 22.7$, 44.0 and 214.2, values very near to once, twice and ten times 22. In all the experiments 180 mols KCl were used as a coagulating agent.

On the other hand *Westgren* and *Reitstötter*[6] found in accordance with the theory, that the rate of coagulation is dependent on the number of particles but not on their size. So the curve for the change of $\Sigma\nu$ with the time is the same for gold sols having the same number of particles per c.cm., but with radii of respectively 76, 96, 120, and 152 μμ. It is remarkable that the theory even holds in the case of ruby glass, a dispersion of gold in borax-glass. When heated the gold coagulates and *Ehringhaus* and *Wintgen*[52] found the decrease of the number of particles in harmony with *von Smoluchowski's* theory.

From all this we may conclude that the mechanism of coagulation with a sol deprived of any stabilizing factor is merely ruled by the probability of collision of the particles and the size of their sphere of attraction for one another.

3. Coagulation of Non-Discharged Particles

Von Smoluchowski[5] has also discussed how the rate of coagulation will be in the case that the particles are not totally discharged. The remaining electric charge will decrease the probability of adhesion, the sphere of attraction will be smaller, it will be even possible that there is no attraction left any more, but that repulsion has come instead of it. In this latter case the sol will of course be stable; therefore we shall consider the case, that only a small electric charge is left, that the rate of coagulation is consequently only somewhat decreased.

Now *von Smoluchowski* thought that in this case the rate of coagulation was governed by quite the same law as when there was no charge whatever, only the time of coagulation would be multiplied by a factor dependent on the charge. For this case he wrote equation (3):

$$\Sigma\nu = \frac{\nu_0}{1 + \varepsilon \frac{t}{T}} \tag{4}$$

in which ε is that factor. This would mean that a calculation of T from the measurements of $\Sigma\nu$ would give constant values, all curves for the rate of coagulation would be "affine," that is to say they become identical when multiplied by a certain factor (viz.: ε).

This point of view of *von Smoluchowski* does not seem improbable at first sight: the remaining charge only diminishes the probability of adhesion by a certain amount, a certain percentage of the collisions will have no effect, but for the rest all will go on in the same way. In the case of complete discharge $\varepsilon = 1$, every collision means coalescence, in the other case $\varepsilon < 1$, indicating that only that part of the number of collisions has such an effect.

However, experiments have not confirmed the theory. *Kruyt* and *van Arkel*[7] made measurements on the rate of coagulation with selenium sol; when they added so much electrolyte that complete discharge took place, that is when $\varepsilon = 1$, measurements gave constant values of T, according to equation (3), but when less electrolyte was added, the calculated value of T (respectively $\frac{\varepsilon}{t}$) was not constant at all. An example is given in Table II.

TABLE II

Selenium sol, average radius of particles: 52 μμ.
Coagulating agent: KCl, 50 mmol. p. L.
Sol concentration: 29.7×10^8 particles p. ccm.

Time in Hours	$10^8 \times$ Number of Particles in 1 c.cm.	Time of Coagulation T
0.00	29.70	—
0.66	20.90	1.5
4.25	19.10	7.6
19.00	14.40	18.0
43.00	10.70	24.0
73.00	7.70	25.0
167.00	6.45	46.0

This rather amazing result was called into question by *Westgren* and *Reitstötter*,[8] as they thought an experimental error had played a part in the affair; but *Kruyt* and *van Arkel*[9] pointed out that their results were correct, and since then others have come to the same conclusion, that formula (4) does not hold for the so-called slow coagulation (cf. next §). Even *Westgren's* own experiments point in the same direction as *van Arkel*[10] calculated from *Westgren's* results with a gold sol after addition of unsufficient NaCl to get rapid coagulation. The numbers are given in Table III.

TABLE III

Gold sol, average radius of particles: 120 μμ.
Coagulating agent: NaCl, 4.8 mmol. p. L.
Sol concentrations: 4.35 × 10^8 particles p. c.cm.

Time in Hours	10^{-8} × Number of Particles in 1 c.cm.	Time of Coagulation T
0.0	4.35	—
0.5	4.01	59
1.0	3.74	61
2.0	3.32	65
3.0	3.28	94
5.0	3.33	160
9.0	3.35	300
28.0	3.20	670

So we see that all investigations carried out by a direct counting of the particles lead to the result that *von Smoluchowski's* theory does not hold in the case of slow coagulation. It seems as if the mechanism of coagulation itself is not the same in slow and in rapid coagulation, or as if ε (cf. equation 4) is again a function of time, what would mean that the electric charge of successively formed particles increases during the process of coagulation; that is, the charge increases while the particles grow. We still lack the experimental data to give a satisfactory explication of the process.

4. Investigations by Other Methods

Counting the particles is a very tiresome and rather dull procedure: *Kruyt* and *van Arkel* [7] for instance had made about 200,000 countings to come to the conclusion given above! As the kinetics of a process is always an important way to reach an insight of its mechanism, several scientists have tried to study the kinetics of coagulation by an easier method.

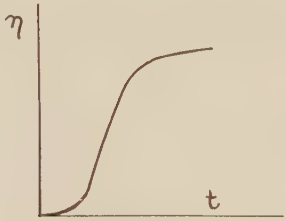

Fig. 2.

Paine [11] studied the rate of coagulation of a copper sol (strictly speaking of a copperoxyd-sol) by titrating samples of the supernatant liquid taken from above the coagulum. *von Smoluchowski* [12] has criticized this method because the stirring, necessary to get a good sediment, affects the kinetics of the process. On the other hand *Jablczynski* [13] in a recent paper and working with a method we shall discuss presently, found stirring had no influence at all on the rate of the process.

Freundlich and his coworkers *Ishizaka* [14] and *Gann* [15] tried to follow the process of coagulation with a $Al(OH)_3$-sol by measuring its viscosity at regular intervals after the addition of the coagulating electrolyte. Their results are of the type of Fig. 2; in this figure the viscosity is given in its relation to time. It can be seen from this graph that after a time of small increase a rapid increase sets in; so, if we assume that viscosity is a measure for the state of aggregation of the particles, one gets the impression that coagulation is an *autocatalytic process.* It is very remarkable that such is the conclusion of *Paine's* work too; and not only of his, but also of *Sven Odén's,*[16] who made investigations very comparable to those of *Paine:* he measured by means of an ingenious apparatus with $BaSO_4$ and other suspensions the amount of the sediment, as it fell out gradually. This amount when graphically represented in connection to time, gives again a graph of the Fig. 2 type.

Such an autocatalytic effect cannot find a proper place in *von Smoluchowski's* theory. He therefore has criticized this kind of investigation and ascribed their results to special conditions caused by the movement in the liquid, either to the flow in the capillary of the viscosimeter or to the stirring; moreover the relation between viscosity and coalescence of the particles is not so simple as supposed in these investigations. Indeed, in the direct measurements of the rate of coagulation by counting the particles, no autocatalytic behavior is found. In the case of the rapid coagulation *von Smoluchowski's* theory is fulfilled and in the case of the slow coagulation *Kruyt* and *van Arkel* found exactly the contrary. From Table 2 it can be seen that the time of coagulation increases gradually, and thus the coagulation going on slower and slower during the whole time of the process.

We are inclined to think *von Smoluchowski* is right and autocatalytic behavior does not set in as long as the assumptions which *von Smoluchowski* premises are fulfilled, viz.: that the particles are subjected to no other movement than such as can be ascribed to the *Brown*ian movement. As soon as stirring, streaming or sedimentation interferes with the process, the larger particles act as a broom and sweep many smaller particles out of the sol when these come into their way.

However, as these complications are quite common facts when we are dealing with a phenomenon of coagulation, they are as important as the academic case discussed in *von Smoluchowski's* theory. Only they complicate the case and make it more difficult for a quantitative interpretation. But as we are dealing with well established facts, we have to take them into account, when we wish to understand the mechanism of coagulation in those cases where these complications set in. And such is the case in a great many of the cases studied in colloid chemistry up to the present.

A third method used in this domain of colloid chemistry is an optical one. *Lottermoser*[17] measured the increase of turbidity when acids were added to the sol of Na_2WO_4; here too one gets the impression of an autocatalytic character of the process. *van Liempt*[18] repeated this investigation, and though he found the same type of phenomenon doubted the reality of the autocatalytic character. *Schoorl*[19] found a similar relation between the refraction of a coagulating protein sol and the time.

Several chemists studied the rate of coagulation with gold sols using a spectro-photometer or a colorimeter. With this last instrument *Hatschek*[20] estimated the percentage of red and blue, as color changes during coagulation of the sol. He tested the applicability of equation (2), supposing $\frac{\nu_1}{\nu_0}$ to be given by the percentage of red in the sol. His result is that the slower the rate of coagulation is the more T increases with time, a conclusion in harmony with *Kruyt* and *van Arkel's* results (cf. Table II). *Anderson*[21] has extended these experiments and has come to the same conclusion. Similar investigations on the congo ruby sol have been done by *Luers.*[22]

Mukherjee and *Papaconstantinou*[23] followed the same process with the spectrophotometer, measuring the absorption at a certain wavelength. They discuss their results in the following ingenious way: If *von Smoluchowski's* theory for slow coagulation were really correct, sols coagulated by different amounts of electrolyte would pass exactly the same stages, only after different times. Now every step is characterized by its absorption; so if we compare the times after which these different sols reach the same absorption there must be a constant relation between these values. At first these scientists found a rather good agreement between their results and the theory, but recently *Mukherjee* and *Majumdar*[24] came to the conclusion that with the As_2S_3 sol this is only the case in the first stage of the process; subsequently the rate becomes smaller and smaller. So their conclusion is again in harmony with that of *Kruyt* and *van Arkel.*

The only investigation in which the applicability of *von Smoluchowski's* theory for slow coagulation is defended is that of *Jablczynski,*[13] but where *Mukherjee* and his coworkers have eliminated the relation between intensity of light and the size of the particles, *Jablczynski* introduces the well-known relation given by Lord *Rayleigh.* However, from the work of *Mie*[25] we know this to be incorrect. Therefore we cannot attribute too much value to this only exception, and so we come to the same conclusion from these indirect measurements as we came to at the end of the preceding paragraph.

The influence of temperature on the kinetics of coagulation has been controlled by *Lachs* and *Goldberg*[53] for the gold-sol in the optical way. From the equations given on page 308 we can deduce easily that the time of coagulation must be proportional to the viscosity and inversely proportional to the absolute temperature. This was confirmed by *Lachs* and *Goldberg.*

5. The Probability of Adhesion

From what has been said in the preceding paragraphs we may conclude that *von Smoluchowski's* theory of the mechanism of coagulation is proved by facts completely in case only the probability of collisions plays a rôle, but that with regard to the probability of adhesion, the phenomena are more complex than foreseen by the theory. Now one could say that a colloidal solution with a probability of adhesion 1 is only the cadaver of a sol, for it is deprived of its vital conditions. So up to now *von Smoluchowski's* theory gives us only

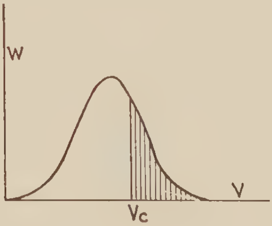

Fig. 3.

a complete theory about a sol's death and we have to look for other ways to understand the sol's physiology!

First of all we may ask with respect to the probability of adhesion: why do only a part of all collisions lead to coalescence? *Freundlich*[26] has given us some insight into this question by the following important train of thought. The particles, when electrically charged, repel each other; therefore they do not approach sufficiently to come reciprocally into their spheres of attraction. If a certain particle has, however, an abnormally great velocity in consequence of its *Brown*ian movement, it could be shot through the field of repulsion into the other's sphere of attraction. Now when we have to do with a more or less stable sol, the mean velocity of a particle of certain mass is governed by temperature; but not all particles of the same size will have exactly the same velocity—deflections of the mean value will occur according to *Maxwell's* partition law. In Fig. 3 the ordinates are the number of particles for each velocity, given on the axis of abscissæ. If a velocity v_c is sufficient to bring a particle so close to another to cause adherence, such will be the case too with particles having a still greater velocity. So the shaded part of the figure will be proportional to the number of particles fit for effective collisions, while the open part of the figure below the curve is proportional to those which will be elastically repelled.

The critical velocity v_c will be greater the higher the repelling tendency, *i.e.*, the higher the electric charge of the particles. Strictly speaking, therefore, a sol is never absolutely stable. On the other hand, without any charge on the particles the whole figure should be shaded; the threshold value is the electrolyte concentration corresponding to such a v and such a charge that in a certain time a beginning of flocculation is just visible; the limit- or flocculation-value is that concentration at which the "critical potential" is reached, viz., when in a certain time complete flocculation is exactly reached.

Now that the exact way of counting particles during flocculation and the other methods discussed above have given insufficient results, to get a good insight into the mechanism of slow coagulation, *i.e.*, in the change of the probability of adhesion, we must utilize other data to control the correctness of our points of view developed in the preceding paragraphs. As long as modern colloid chemistry has been studied, much attention has been paid to the flocculation concentration of different electrolytes. From the elder measurements of *Schulze, Linder* and *Picton* and so many others, *Freundlich*[27] deduced his fundamental theory of the relation between adsorbability, valency and flocculation, discussed elsewhere in this book; *Hardy's*[2] and *Burton's*[28] results on the narrow relation between charge and stability of course is the foundation on which that theory is built.

Now in reality this whole theory of *Freundlich* is a discussion of the change of the probability of adherence by the electric conditions, as they are changed by adding electrolytes. His starting-point can be formulated thus: to reach such a probability of adherence, that complete flocculation is reached within a certain time, equimolecular amounts of the flocculating ion must be adsorbed. However there is an unmentioned supposition, viz., that the probability of collision remains unchanged. Now this is really the case in the greater part of investigations carried out in this domain; but there are cases in which both variables change, and then facts appear which can be explained only from the points of view developed above. In the next paragraph we shall discuss the relation between the flocculation value and the concentration of the sol.

6. THE CONNECTION BETWEEN THE CONCENTRATION OF A SOL AND ITS FLOCCULATION VALUE

Let us compare a sol and another, made by diluting part of the former in a ratio 1 : 1; so the latter will contain per ccm. half the number of particles compared with the former. Let us call the flocculation value of the first sol for a certain electrolyte γ_1; when we added to a liter of that sol γ_1 mmols of that electrolyte, an amount of α mmols will be adsorbed and χ_1 mmols will remain in the solution, while $\gamma_1 = \chi + \alpha$. To flocculate the second sol, every particle must adsorb the same quantity, and as there are only half the number of particles only $\frac{1}{2}\alpha$ will be adsorbed. As in both cases the adsorbed mass per cm.^{2} is the same, the concentration of the external phase will be both times χ. The flocculation value of the second sol, γ_2, will be therefore $\gamma_2 = \chi + \frac{1}{2}\alpha$. This train of thought would lead to the conclusion that the flocculation value is the lower the more dilute the sol is.

Kruyt and *van der Spek* [29] checked this theory in the case of the As_2S_3 sol and found it correct for the barium and aluminium ion, but with the potassium ion just the reverse appeared: the flocculation value increased with dilution. The line of thought given above can explain this fact. Up to now we have reasoned as if we had to bring both sols to the same probability of adherence; this would be true only if the probability of collision were unchanged by dilution. However, such is of course not the case, for by dilution the particles are brought further from one another and in consequence the number of collisions per unit of time is decreased. To get the same effect of coagulation in the same time, it will be necessary to compensate the decreased probability of collision by an increased probability of adherence, *i.e.*, by adding more electrolyte to increase the adsorbed amount of the flocculating agent and to lower the electric charge of the particles by doing so.

So we have met with one tendency affecting decrease and one affecting increase of the flocculation concentration as a consequence of dilution of the sol. Which will be predominant in a certain case? With the potassium we know from *Freundlich's* [27] theory that α (and $\frac{1}{2}\alpha$) is only a small part of γ and therefore of χ. Consequently the decreasing effect will be only small in the case of an ion of low valency. On the other hand we know from the investigations of *Elissafoff* [30] on electroendosmosis, from those of *Kruyt* [31] on streaming potentials and from those of *Powis* [32] on cataphoresis, that a decrease of charge by a monovalent ion requires a rather high amount of that ion. So we see that with an ion of low valency the increasing effect will predominate, whilst another effect will set in with ions of higher valency. In Fig. 4 results of *Kruyt* and *van der Spek* [29] are represented; the flocculation value for the original sol is taken as unity for each electrolyte. These results illustrate the given theory: the monovalent ion showing an increase, the trivalent ion a decrease in consequence of dilution; the divalent ion takes a middle position, here showing a decrease, whilst *Burton* and *Bishop* [33] found a small increase with Ca and Zn. On the other hand *Burton* and *McInnes* [34] found results practically concordant with those of *Kruyt* and *van der Spek,* also *Freundlich* and *Loening* [35] for the silver sol, and *Freundlich* and *Scholz* [36] for the sulphur sol. The results of *Mukherjee* and *Sen* [37] are also in agreement with this theory. With positively charged sols *Burton* and *Bishop* [33] found that the sol of CuO gave flocculation-values increasing with dilution in the case of the monovalent Cl-ion, constant values for the divalent SO_4-ion and decreasing for the trivalent PO_4-ion. For the sol of Fe_2O_3 *Kruyt* and *van der Spek*,[29] as well as *Murphy* and *Mathews*,[38] found decreasing values for the three ions just mentioned; at the other hand *Kruyt* and *van Arkel*[39] found with the gold-sol increasing values with K, Ba and Al, decreasing values only with the quadrivalent Th-ion. However, these somewhat divergent results do not contradict the theory given above: specific conditions of each sol will regulate the valency of the added electrolyte at which the increasing or the decreasing influence will predominate. But when experimenting with flocculating ions with increasing order of valency, as soon as the decrease sets in, such must remain the case for all ions of still higher valency; and this is proved in all the investigations carried out up to now.

This specificity of different sols touches again the question as to what the correlation is between the electric charge and the probability of adhesion. Though up to the present we do not know the exact quantitative relation between these two, the results we have just discussed can give us some information.[40] In Fig. 5 three diagrams are combined: I. gives the well known *Freundlich*-diagram,[27] explaining the *Schulze-Hardy*-rule (to combine it with II it has been placed upside down); II gives the relation between the concentration c of an electrolyte and the potential ζ at a surface (*Kruyt*[31]), and III must give us the relation between the probability of adhesion K and the potential ζ, *i.e.*, the relation we wish to know. Now let the horizontal line in parts II and III be drawn just at the critical potential of the sol we are discussing, say the As_2S_3-sol. Why now is the curve in III drawn with the shape of our figure? K can vary from nearly 0 (at a high value of ζ) to 1 (at $\zeta = 0$). Now we know that addition of small amounts of an electrolyte has hardly any influence on the sol; therefore the K-line near to $K = 0$ is drawn convex to the ζ axis. On the other hand at potentials below the critical value, all sols coagulate almost spontaneously; therefore the curve is drawn concave in the neighborhood of $K = 1$. So we get a curve with a point of inflection. Now the influence of an electrolyte on the change of ζ depends on the valency of the active ion (part II of our figure), this influence being larger the higher the valency. The influence of the change of ζ on the flocculation, however, depends on the shape of the $K\zeta$-figure. It was just this influence that had to counteract in our

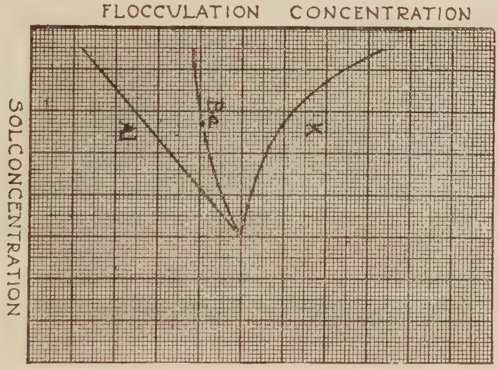

Fig. 4.

theory given above, the probability of collision when decreased by the dilution of the sol. If now part II of our Fig. 5 is of general applicability (and we have many reasons to assume that it is) the specific behavior of different sols must be sought in their $K\zeta$-curve. Probably Fig. 6 gives the $K\zeta$-curve for a gold-sol: It points out the difference of a gold-sol compared to the As_2S_3-sol of Fig. 5; with this sol a slight augmentation of the concentration of a bivalent or trivalent ion causes a great change of ζ and the same of K; with the gold-sol, however, these ions change ζ in the same way, but that change of ζ changes K very little, at least in the neighborhood of the critical potential. To increase K sufficiently a still greater change of K and therefore of ζ is wanted and only the quadrivalent Th-ion can effect this.

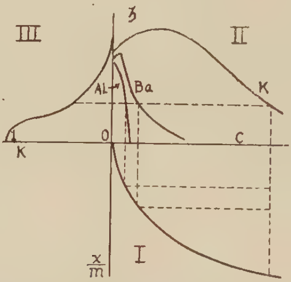

FIG. 5.

So we get a little insight into this instance of the mechanism of coagulation in an indirect way. It is interesting that *Freundlich*[26] by quite another train of thought has come to a similar relation between electric charge and probability of adhesion; only he uses quite other words. In Fig. 3 we learned his important theory about the influence of the critical velocity: we saw that those particles would adhere which had a velocity greater than v_c, necessary to shoot through the repulsion area. The greater the charge, the greater the critical v. The shaded part of Fig. 3 compared to the open part gave the relation between the adhering and the total number of particles, but this relation is nothing else but the probability of adherence. Now *Freundlich*[26] has given a graphical representation as to how this relation varies with v_c

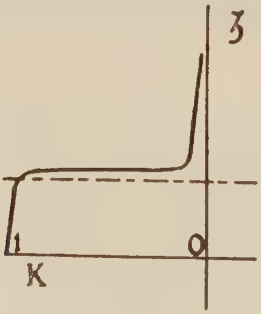

FIG. 6.

after the application of calculus to the problem: the result is a so-called Gothic-arch curve, just as the $K\zeta$-line in our Fig. 5.

The train of thought given above enables us to come to a better understanding of the terms flocculation-value, critical potential, rapid coagulation, etc. The S-shape of the $K\zeta$-figure shows us that there is always a certain range of ζ-values, where a small change of ζ brings about an enormous change of the probability of adhesion. This change of ζ is caused by the concentration of the added electrolyte; therefore we can say as well that there is a certain range of electrolyte concentrations where a small change brings about an enormous change of K and consequently of the rates of coagulation. Within that range the time of coagulation changes from several hours (even days) to some minutes or seconds. Here is the transition from slow to rapid coagulation; here lies that concentration, where coagulation is complete within a short time (two hours for an As_2S_3- sol, five minutes for a gold-sol, etc.) while a small diminution of the concentration brings about an enormous increase of time to come to same endpoint: so here lies the flocculation value. Therefore we can say, the flocculation value lies in the transition interval between slow and rapid coagulation; it cannot be defined more sharply, as it is a function both of the probability of collision and that of adhesion, as we discussed above. The same can be said of the critical potential, being the ζ-value, which corresponds in part II of Fig. 5 to the c-value of the flocculation value. As we say in Figs. 5 and 6, the S-curve is in one case much steeper than in another, this being, of course, of great influence on the exactitude with which the flocculation value and the critical potential can be determined. (Cf. the papers of *Powis* [32] and of *Limburg* [51] from this point of view.)

7. OTHER FACTORS THAN ELECTRIC CHARGE EXERTING INFLUENCE UPON THE PROBABILITY OF ADHESION

I. Hydration.

Up to now we have considered the electric charge as the only factor exerting influence upon the probability of adhesion. With mere suspensoids this is indeed the case; but with lyophilic sols, as with emulsoids, another factor is of equal influence on this probability, viz., the hydration. To get an insight into the mechanism of coagulation of lyophilic sols we shall have to consider the influence of hydration first.

The electric charge of a sol of agar-agar,[41] of starch [42] or of gelatine [43] can be taken away fully without causing the least indication of coagulation. If we add electrolytes to such a sol in concentrations of some milli-equivalents, which would be sufficient to flocculate a suspensoid sol, no flocculation sets in. Nevertheless the particles have lost their charge, as can be seen from cataphoretic measurements, but, as these are not easy with emulsoid sols, still better by the observation of the disappearance of the effect, which *von Smoluchowski* has called the "quasi-viscous effect" but what we may call the *electro-viscous effect;* [44] the electric charge gives namely an increase of the viscosity of the sol.

The reason that a discharged lyophilic sol does not coagulate cannot be sought in the probability of collision, which cannot be different from that of a suspensoid sol, but there must be some factor maintaining the stability of the sol by lowering the probability of adhesion, even when no electrical charge is left. It is obvious that this factor is the hydration of the particles, for the discharged sol flocculates as soon as we add dehydrating substances such as alcohol, sulfuric acid, acetic acid, acetone, etc. Neutral salts too have a dehydrating influence in consequence of the hydration of their ions (*Washburn*[45]), this influence being dependent of the position of these ions in the so-called lyotropic or *Hofmeister* series. Such salts, like $MgSO_4$ and $(NH_4)_2SO_4$, can cause flocculation or "salting out," as it is usually called, by first discharging and then dehydrating the particles. *Kruyt* and *de Jong*[41] have proved this for the sol of agar by studying the viscosity of the sol.

The viscosity of a dispersed system is governed by *Einstein's* law:[46]

$$\eta_s = \eta_o \left(1 + \frac{5}{2}\varphi\right) \quad \text{or} \quad \frac{\eta_s}{\eta_o} - 1 = \frac{5}{2}\varphi$$

when η_s is the viscosity of the sol, η_o that of the external phase and φ the total volume of the internal phase. Therefore $\frac{\eta_s}{\eta_o} - 1$ is a measure for the active volume of the dispersed phase and consequently indicates the degree of hydration. Only *von Smoluchowski*[47] pointed out that *Einstein's* relation is valid for only electrically uncharged particles, the complete expression being

$$\frac{\eta_s}{\eta_o} - 1 = \frac{5}{2}\varphi\left\{1 + \frac{1}{\varkappa r^2 \eta}\left(\frac{\zeta D}{2\pi}\right)^2\right\}$$

when r is the radius of the particles, ζ the potential in the double layer, D the dielectric constant and $\varkappa$ the specific conductivity of the system. So when adding small traces of an electrolyte (the necessary quantity being dependent of the valency of the ion with a sign opposite to that of the particle) *Kruyt* and *de Jong*[41] first noticed a decrease of the viscosity caused by the removal of the electroviscous effect. When thereupon a dehydrating agent was added, whether alcohol or a $MgSO_4$ in concentrations up to 1-molar solution, a continuous decrease of the relative viscosity resulted and at a certain degree of dehydration flocculation set in. In Fig. 7 these results are represented graphically. When at the other hand first alcohol is added and almost complete dehydration reached in that way but leaving the electric charge unchanged, no flocculation occurs, the sol merely changing its character from lyophilic to lyophobic.

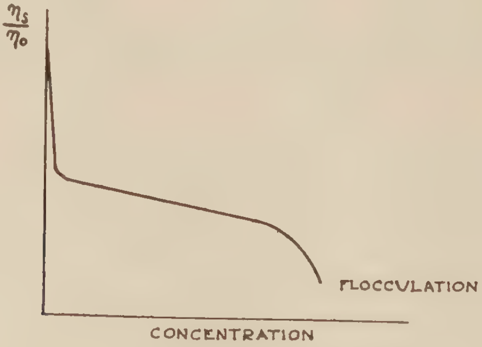

Fig. 7.

These results lead us to this conclusion: The probability of adhesion in a lyophilic sol is not only dependent on its electric charge but also on its hydration, both being factors which counteract adhesion. As we know "critical potential" (*Powis* [32]) for a sol with a stability depending only on its electric charge, we can speak of "critical hydration" for a sol depending only on its hydration. With a sol provided with both stabilizing factors it is of course possible that it be still stable when both these critical values are passed, but in such a way that both factors together give a sufficiently low probability of adhesion to the sol. In such a case the degree of discharge, necessary to cause flocculation, will be dependent of the present hydration, and on the other hand the degree of dehydration will be dependent on the present charge. An example of this last case we meet with the so-called alcohol-numbers [43, 48] for the flocculation of gelatin sols, which are a minimum when the sol is uncharged ($p_H = 4.7$) but rising when a positive or a negative charge is given to the sol.[43]

So we see that the mechanism of coagulation with a lyophilic sol, though quite comparable with that of a suspensoid sol, is only one degree more complicated: In both cases we can divide the mechanism into two parts: the mere kinetic, governed by the probability of collision, and the other, dealing with the effect of those collisions, governed by the probability of adhesion. However, where this last is only a function of the particles' charge with suspensoids, with emulsoids we have to take both electric charge and hydration into account.

II. Protective Action.

It is a well-known fact that the coagulation of a supensoid can be retarded considerably by the addition of certain emulsoids.[49] When we add gelatin to a gold sol, the dispersity of the gold sol is not changed, nor is the viscosity changed by the extremely small gelatin concentration which actually causes an enormous protective action; thus, the probability of collision is unchanged, and the reason for the retardation must be sought in a decrease of the probability of adhesion. However, there is no appreciable increase of the electric charge as *Freundlich* and *Loening* [35] pointed out with the Ag-sol. From the work of *Zsigmondy* [50] we know that the protective colloid is adsorbed by the gold, so the gold particles become surrounded by a layer of gelatin particles and we saw in the preceding paragraph that these bear the water of hydration as a protector against coalescence, *i.e.*, as a factor diminishing the probability of adhesion. So the gold particles get their share in this decrease of the probability of adhesion and consequently the problem of protective action is reduced to that of hydration, discussed in the preceding paragraph.

From this we can expect that the rate of coagulation is diminished by a protective colloid, but that the general behavior of the process is not changed by it. Indeed, *Luers* [22] found this to be the case with the sol of Congo red, when gelatin was added and *Paine* and *Evans* [11] found the same with the sol of copper oxide, when starch was added.

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Theory of the Opalescence of Homogeneous Liquids and Mixtures of Liquids in the Vicinity of the Critical State [*]

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Smoluchowski has shown, in an important theoretical paper,[†] that the opalescence of liquids in the vicinity of the critical state and of mixtures in the vicinity of the critical solution point can be readily explained from the point of view of the molecular theory of heat. This explanation is based on the following general consequence from *Boltzmann's* Entropy-Probability principle: an isolated physical system passes during an infinite time through all the states which are consistent with the (constant) value of its energy. But the statistical probability of state differs here appreciably from zero only in the case when the work which, according to the laws of thermodynamics, must be applied in order to bring the system to the state considered, from the state of ideal thermodynamic equilibrium, has the same order of magnitude as the kinetic energy of a monatomic gas molecule at the corresponding temperature.

Therefore, if such a small amount of work is sufficient to bring about, in a portion of the liquid of the order of magnitude of a cube whose edges are equal to the wave length, a density which differs appreciably from the average density of the liquid (or a proportion of the components of the mixture which differs appreciably from the average proportion of the mixture) an opalescence (Tyndall phenomenon) must appear. *Smoluchowski* showed that this condition is actually fulfilled in the vicinity of the critical state; he gave, however, no exact calculation of the amount of light scattered laterally by the opalescence. It is the purpose of this paper to fill in this gap.

§ 1. Generalities Concerning *Boltzmann's* Principle.

Boltzmann's principle can be written down in the form of the following equation:

$$S = \frac{R}{N} \lg W + \text{const.} \qquad (1)$$

where

R = the gas constant,
N = the number of molecules in one gram molecule,
S = the entropy,
W = the quantity usually referred to as "the probability" of the state possessing the entropy value S.

It is customary to let W be equal to the number of possible different ways (complexions) in which the state under consideration may be conceived as realized, a state being incompletely characterized by observable parameters of a system in the sense of the molecular theory. In order to be able to calculate W we have to use a *complete* theory (*e.g.*, a complete molecular-mechanical theory) of the system which we have in view. It therefore appears to be doubtful whether, if we accept this point of view, the *Boltzmann* principle alone, *i.e.*, without a complete theory—be it a molecular-mechanical theory or any other theory which depicts completely the elementary phenomena (elementary theory)—has any significance at all. Equation (1) without the addition of an elementary theory, or—as we may put it—regarded from the phenomenological point of view, appears to be meaningless.

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[*] Translated by Dr. G. Y. Rainich, Johns Hopkins University, Baltimore, Md.

[†] *Annalen der Physik.*, 33, pp. 1275-1298, Dec. 20, 1910.

[‡] M. v. Smoluchowski, *Ann d. Phys.*, 25, pp. 205-226, 1908.

But *Boltzmann's* principle assumes a meaning independent of any elementary theory, if we take over from molecular kinetics the theorem that the irreversibility of physical phenomena is only apparent and apply it, in a generalized form, to our case.

Let us, then, assume that the state of a system is determined—in the phenomenological sense—by the variables $\lambda_1 \ldots \lambda_n$ which, in principle at least, can be observed. With every state Z is associated a combination of values of these variables. If the system is isolated, the energy does not change; and, in general, the energy is the only function of the variables which does not change. We consider all the states consistent with the amount of energy which the system possesses and denote them by $Z_1 \ldots Z_l$. If we do not accept as a principle the irreversibility of processes, the system will pass, as time goes on, again and again through the states $Z_1 \ldots Z_l$. Under this assumption we may speak of the probabilities of different particular states in the following sense: if we imagine that the system was observed during an immense interval of time Θ and it was found that out of this whole time, the system was in the state Z_1 during a time τ_1, then the fraction τ_1/Θ is the probability of the state Z_1, and similarly for the other states. According to *Boltzmann* the apparent irreversibility is accounted for by the fact that different states have different probabilities, and that it is more probable that the system will pass into a state of higher probability if it just is in a state whose probability is relatively low. The fact that the phenomena seem to follow strictly the law of irreversibility is due to the circumstance that the probabilities of different states are of *different orders of magnitude*, so that among all the states which are in the vicinity of a given state Z_1 there is *one* state, Z_2, which almost certainly will follow Z_1, because Z_2 is vastly more probable than the others.

It is the probability introduced in the way just outlined (in this case no elementary theory is required for its determination), which is connected to the entropy by the relation (1). We see easily that relation (1) must, in fact, hold for the probability so defined. The entropy is namely a function which (in the domain of applicability of thermodynamics) never decreases while the system remains isolated. There are still other functions having the same property but all of them are, if the energy is the only function of the system which does not change with time, of the form $\varphi(S, E)$, $\partial\varphi/\partial S$ being always positive. Since the probability W also is a function which does not decrease in any process, W must be a function of S and E alone or—if only states with the same energy are being compared—a function of S alone. The fact that the relation expressed by Equation (1) is the only possible relation connecting W and S can be proved, as is well known, using the theorem according to which the entropy of a system consisting of partial systems is equal to the sum of entropies of the constituent systems. In this way Equation (1) can be proved for all states Z which belong to the same value of energy.

At first the following objection against this interpretation of *Boltzmann's* principle presents itself. What we have to speak of is not a statistical probability *of a state* but a probability *of a region of states*. Such a region is given by a part G of the "energy surface" $E(\lambda_1 \ldots \lambda_n) = 0$. It is obvious that W tends toward zero together with the magnitude of the part chosen. Therefore Equation (1) would have no meaning whatsoever but for the fact that the relation between S and W is of a very special type. Thus it so happens that lg W appears in (1) multiplied by a very small factor R/N. Assume that we have found the value of W for a region G_w whose dimensions are of about the size of the limit of perceptibility; lg W will have a definite value. Should we make our region, say, e^{10} times smaller, the right hand side would, as a consequence of this change of the region, decrease only by a vanishingly small quantity $10(R/N)$. If therefore we take the dimensions of our region small in comparison with observable dimensions, and at the same time large enough to make $R/N \lg G_W/G$ numerically negligible, then Equation (1) has a sufficiently precise meaning.

So far it had been assumed that $\lambda_1 \ldots \lambda_n$ characterize *completely* the state of the system considered from the phenomenological point of view. But Equation (1) retains its meaning without restrictions also in the case when we are concerned with probabilities of a state which is not completely determined in the phenomenological sense, viz., which is characterized by definite values $\lambda_1 \ldots \lambda_\nu$ (with $\nu < n$) only while the values of the remaining λ are left undetermined. Among all the states with given $\lambda_1 \ldots \lambda_\nu$ those will be by far the most frequent for which the entropy of the system (the values $\lambda_1 \ldots \lambda_\nu$ remaining constant) will be maximum. Equation (1) holds in this case for *this* maximal value of entropy and for the probability of *this* state.

§ 2. On the Deviations from a State of Thermodynamic Equilibrium.

We are now going to draw some conclusions from Equation (1) concerning the connection between the thermodynamic properties of a system and its statistical properties. Equation (1) gives immediately the probability of a state if its entropy is given. But we have seen that this relation is not an exact one: if S is known (1) permits us to calculate only the order of magnitude of W for the corresponding state. Nevertheless it is possible to deduce from (1) exact relationships governing the statistical behavior of the system, viz., for the case when the region of the variables (characterizing the state) for which W has the values to be considered, may be taken as infinitely small.

From Equation (1) it follows

$$W = \text{const.}\, e^{\frac{N}{R} S}.$$

This equation holds, as far as orders of magnitude are concerned, if we assign to every state Z a small region of the order of magnitude of the limit of observable quantities. To determine the constant, we use the fact that for the maximal value (S_o) of entropy, the probability must be of the order of magnitude of unity, so that we have for the orders of magnitude

$$W = e^{\frac{N}{R}(S - S_o)}.$$

Hence it follows that the probability dW for the quantities $\lambda_1 \ldots \lambda_n$ to have values between λ_1 and $\lambda_1 + d\lambda_1 \ldots \lambda_n$ and $\lambda_n + d\lambda_n$, is of the order of magnitude *

$$dW = e^{\frac{N}{R}(S - S_0)} \, . \, d\lambda_1 \ldots d\lambda_n;$$

this is true in the case when the system is only incompletely characterized by the $\lambda_1 \ldots \lambda_n$ (in the phenomenological sense).† To be precise, dW differs from the expression just given by a factor f, so that we have to put

$$dW = e^{\frac{N}{R}(S - S_0)} \, . \, f \, . \, d\lambda_1 \ldots d\lambda_n.$$

Here f is a function of the $\lambda_1 \ldots \lambda_n$ and has such an order of magnitude as not to affect the order of magnitude of the right hand side.‡

We proceed now to find an expression for dW in the immediate neighborhood of a maximum of entropy. If the Taylor series converges in the region in question, we have to put

$$S = S_0 - \tfrac{1}{2}\Sigma\Sigma s_{\mu\nu}\lambda_\mu\lambda_\nu + \ldots$$

$$f = f_0 + \Sigma\lambda_\nu\left(\frac{\partial f}{\partial \lambda_\nu}\right) + \ldots$$

the state which corresponds to maximum entropy being assigned the values $\lambda_1 = \lambda_2 = \ldots = \lambda_n = 0$ of the variables. The double sum in the expression for S is essentially positive since we are dealing with a maximum of entropy. We may, therefore, introduce instead of the λ's new variables in such a way as to have only a simple sum, viz., the sum of the squares of the new variables, which we denote again by $\lambda_1 \ldots \lambda_n$. We obtain thus

$$dW = \text{const.}\, e^{-\frac{N}{2R}\Sigma s_\nu \lambda_\nu^2 + \ldots} \, . \left[f_0 + \Sigma\left(\frac{\partial f}{\partial \lambda_\nu}\lambda_\nu\right)\right] d\lambda_1 \ldots d\lambda_n.$$

The terms which appear in the exponent are multiplied by the very large number N/R. For small values of the λ's corresponding to states which do not differ appreciably from the state of thermodynamic equilibrium the exponential factor will therefore, in general, be negligible. For such small values of the λ's the factor f may be replaced by the value f_0 which corresponds to the state of thermodynamic equilibrium. In all these cases when the variables differ only slightly from the values which they assume in the ideal case of thermodynamic equilibrium we may write for our formula

$$dW = \text{const.}\, e^{\frac{N}{R}(S - S_0)} \, . \, d\lambda_1 \ldots d\lambda_n. \tag{2}$$

For such small deviations from the thermodynamic equilibrium, as those which we have to deal with in our case, the quantity $S - S_0$ has an intuitive interpretation. If we think of the states in which we are interested here as being brought about in a reversible way by external influences, then, accord-

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* We shall assume that the regions of observable quantities λ have finite extensions.

† In the other case the manifold of all possible states would be only $(n - 1)$-dimensional in consequence of the energy principle.

‡ We do not know anything about the orders of magnitude of the derivatives of f with respect to the λ's. But we shall assume in what follows that these derivatives are of the same order of magnitude as f itself.

ng to thermodynamics, for every elementary process there must hold the nergy equation

$$dU = dA + TdS$$

if U denotes the energy of the system and dA the elementary work which is being applied to it. We are interested only in states which can be assumed by an isolated system, in states, that is, which belong to the same energy value. For such a transition from one state to a neighboring state we have $dU = 0$. We further make only a negligible error if we substitute in the above equation the temperature T_o of the thermodynamic equilibrium for T. This equation becomes then

$$dA + T_o\, dS = 0$$

or

$$\int dS = S - S_o = -\frac{1}{T_o} A, \tag{3}$$

and A denotes the work which has to be used, according to thermodynamics, in order to bring the system from the state of thermodynamic equilibrium to the state under consideration. We may write, therefore, Equation (2) in the form

$$dW = \text{const.}\, e^{-\frac{N}{RT_o}A}\, d\lambda_1 \ldots d\lambda_n. \tag{2a}$$

We suppose that the parameters λ are chosen in such a way that they vanish for the state of thermodynamic equilibrium. In a certain neighborhood it will be possible to use the Taylor series for A and by appropriate choice of the λ's we can give this series the form $A = \frac{1}{2}\Sigma a_\nu \lambda_\nu^2 +$ terms of degree higher than two in the λ's where all the a_ν are positive. Since, further, the quantity A appears in Equation (2a) multiplied by a very large factor N/RT_o, the exponential factor will be appreciably different from zero in general only for very small values of A and, therefore, also for very small values of λ. For such small values of the λ's the terms of higher degrees in the expression of A will furnish contributions which are negligible in comparison with terms of the second degree. If this is the case we can write, instead of (2a), the equation

$$dW = \text{const.}\, e^{-\frac{N}{2RT_o}\Sigma a_\nu \lambda_\nu^2}\, d\lambda_1 \ldots d\lambda_n, \tag{2b}$$

an equation which has the form of the *Gaussian* law of errors.

We are going to limit ourselves in the present paper to the consideration of this important special case. It follows from (2b) immediately that the average value of the work A_ν which corresponds to the parameter λ_ν is

$$\overline{A_\nu} = \overline{\tfrac{1}{2}a_\nu \lambda_\nu^2} = \frac{RT_o}{2N}. \tag{4}$$

This average work is thus equal to a third of the average kinetic energy of a molecule of a monatomic gas.

§ 3. On the Deviations of the Spatial Distribution of Liquids and Mixtures of Liquids from Homogeneous Distribution.

We denote by ρ_o the average density of a homogeneous substance, or the average density of one of the components of a binary mixture of liquids.

Due to the irregularity of thermal agitation, the density ρ at a point of the liquid will be in general different from ρ_o. If the liquid is contained in a cube which is given, for certain axes of coördinates, by

$$0 < x < L,$$
$$0 < y < L,$$

and

$$0 < z < L,$$

we may put for inner points of this cube

$$\rho = \rho_o + \Delta,$$
$$\Delta = \sum_{\rho}\sum_{\sigma}\sum_{\tau} B_{\rho\sigma\tau} \cos 2\pi\rho \frac{x}{2L} \cos 2\pi\sigma \frac{y}{2L} \cos 2\pi\tau \frac{z}{2L}. \tag{5}$$

The quantities ρ, σ, τ denote positive integers. But we have to take into consideration the following.

Strictly speaking there is no such thing as density of a liquid at a point; we may speak only of the average density in a region whose dimensions are large compared to the average distance between neighboring molecules. Therefore, the terms of the above expansion in which one of the numbers ρ, σ, τ exceeds a certain limit will have no physical meaning. We shall see in what follows, however, that this circumstance is of no importance here.

The quantities $B_{\rho,\sigma,\tau}$ vary with time in such a way that their averages are zero. We are interested in the statistical laws which govern the quantities B. These play the rôle of the parameters λ of the preceding section which determine the state of our system from the phenomenological point of view.

According to the preceding section, we shall find these statistical laws by expressing the work A as a function of the quantities B. We can do this in the following way. If $\varphi(\rho)$ denotes the work which must be done in order to bring isothermally a unit of mass of the average density ρ_o to the density ρ, the corresponding work for the mass $\rho d\tau$, which is present in the element of volume $d\tau$, has the value

$$\rho\varphi d\tau,$$

and, therefore, for the whole cube of liquid its value is

$$A = \int \rho \,.\, \varphi \,.\, d\tau.$$

We will have to assume that the deviations Δ of density from the average density are very small and make

$$\rho = \rho_o + \Delta,$$
$$\varphi = \varphi(\rho_o) + \left(\frac{\partial\varphi}{\partial\rho}\right)_o \Delta + \tfrac{1}{2}\left(\frac{\partial^2\varphi}{\partial\rho^2}\right)_o \Delta^2 + \ldots .$$

It follows from this, since $\varphi(\rho_o) = 0$ and $\int \Delta d\tau = 0$,

$$A = \left(\frac{\partial\varphi}{\partial\rho} + \tfrac{1}{2}\rho\frac{\partial^2\varphi}{\partial\rho^2}\right)\int \Delta^2 d\tau,$$

where the subscript zero is left out for the sake of simplicity. We neglected, in the integrand, terms of the third and higher degrees; this is permitted obviously only when

$$\frac{\partial\varphi}{\partial\rho}+\tfrac{1}{2}\rho\frac{\partial^2\varphi}{\partial\rho^2}$$

is not too small and the terms which are multiplied by Δ^3, etc., are not too large. But according to (5), we have

$$\int\Delta^2 d\tau=\frac{L^3}{8}\sum_\rho\sum_\sigma\sum_\tau B^2_{\rho\sigma\tau}$$

because the volume integrals involving products of two different Fourier coefficients vanish. We have thus,

$$A=\left(\frac{\partial\varphi}{\partial\rho}+\tfrac{1}{2}\rho\frac{\partial^2\varphi}{\partial\rho^2}\right)\frac{L^3}{8}\sum_\rho\sum_\sigma\sum_\tau B^2_{\rho\sigma\tau}\,.$$

If we express the work which it is necessary to apply in order to bring a unity of mass from the state of thermodynamic equilibrium to a state when it has a definite density ρ as a function of the specific volume $1/\rho=v$, i.e., if we put

$$\varphi(\rho)=\psi(v),$$

we obtain a simpler expression

$$A=\frac{L^3}{16}v^3\frac{\partial^2\psi}{\partial v^2}\sum_\rho\sum_\sigma\sum_\tau B^2_{\rho\sigma\tau},\tag{6}$$

where v and $\partial^2\psi/\partial v^2$ stand for the values which these quantities take for the state of ideal thermodynamic equilibrium. We notice that only the squares of the coefficients B appear in the expression for A, but not the products of different B's. The quantities B are therefore parameters of the same type which appear in the Equations (2b) and (4) of the preceding section; hence we have it that the B's follow (independently one from the other) the Gaussian law of errors, and Equation (4) gives immediately

$$\frac{L^3}{8}v^3\frac{\partial^2\psi}{\partial v^2}\overline{B^2_{\rho\sigma\tau}}=\frac{RT_o}{N}.\tag{7}$$

We succeeded thus in determining completely, that is in reducing to a function ψ, which can be found thermodynamically, the statistical properties of our system.

We must remark that it is permissible to neglect terms with Δ^3, etc., only when $d^2\psi/dv^2$ is not too small, for the ideal thermodynamic equilibrium; and, of course, we cannot neglect these terms when $d^2\psi/dv^2$ vanishes as is the case for liquids and mixtures of liquids which are in the critical state. In a certain (very small) neighborhood around the critical state, the formulas (6) and (7) do not hold. But there are no *fundamental* difficulties which would prevent us from extending the theory by taking into account the terms of higher degree in the coefficients.*

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* Cf. M. v. Smoluchowski, *loc. cit.*, p. 215.

§ 4. Calculation of the Amount of Light which is Deflected by an Infinitesimally Inhomogeneous Absorptionless Medium.

After having determined on the basis of *Boltzmann's* principle the statistical law which governs the variation in space of density for a single substance or of the proportion of components for a mixture, we pass now to the study of the influence which the medium exercises on a ray of light passing through it.

Let $\rho = \rho_0 + \Delta$ again denote the density of the medium at a given point; or, if we deal with a mixture, the density of one of its components. Let the ray of light which we consider be monochromatic. The medium may be characterized with respect to it by the index of refraction g or by the apparent dielectric constant ε which belongs to the corresponding frequency and which is connected with the index of refraction by the relation $g = \sqrt{\varepsilon}$. We put

$$\varepsilon = \varepsilon_0 + \left(\frac{\partial \varepsilon}{\partial \rho}\right)_0 \Delta = \varepsilon_0 + \iota; \qquad (8)$$

i, as well as Δ, are to be considered as infinitesimal quantities.

The electric and magnetic force vectors **E** and **H** satisfy at each point the *Maxwell* equations, which—since we may neglect the influence of the time derivative of ε on the light—take the form

$$\frac{\varepsilon}{c}\frac{\partial \mathbf{E}}{\partial t} = \text{curl } \mathbf{H}, \qquad \text{div } \mathbf{H} = 0,$$

$$\frac{1}{c}\frac{\partial \mathbf{H}}{\partial t} = -\text{curl } \mathbf{E}, \qquad \text{div } (\varepsilon \mathbf{E}) = 0$$

where c is the velocity of light in vacuo. Eliminating **H** we obtain from this

$$\frac{\varepsilon}{c^2}\frac{\partial^2 \mathbf{E}}{\partial t^2} = \Delta \mathbf{E} - \text{grad div } \mathbf{E}, \qquad (9)$$

$$\text{div } (\varepsilon \mathbf{E}) = 0. \qquad (10)$$

Let now $\mathbf{E}_0$ be the electric field of a light wave, as it would be if ε would not vary in space, or, we shall say: the field of the exciting light wave. The actual (total) field **E** will differ from $\mathbf{E}_0$ by an infinitesimal vector **e**, the field of opalescence, so that we have to put

$$\mathbf{E} = \mathbf{E}_0 + \mathbf{e}. \qquad (11)$$

If we substitute the expressions (8) and (11) for ε and **E** into (9) and (10), take into account that $\mathbf{E}_0$ satisfies *Maxwell's* equations with the fixed value of the dielectric constant ε_0, and neglect infinitesimals of the second order, we obtain

$$\frac{\varepsilon_0}{c^2}\frac{\partial^2 \mathbf{e}}{\partial t^2} - \Delta \mathbf{e} = -\frac{1}{c^2}\,\iota\,\frac{\partial^2 \mathbf{E}_0}{\partial t^2} - \text{grad div } \mathbf{e}, \qquad (9a)$$

$$\text{div } (\iota \mathbf{E}_0) + \text{div } (\varepsilon_0 \mathbf{e}) = 0. \qquad (10a)$$

If we develop (10a) and use the fact that div $\mathbf{E}_0 = 0$ and grad $\varepsilon_0 = 0$, we get

$$\text{div } \mathbf{e} = -\frac{1}{\varepsilon_0}\mathbf{E}_0 \text{ grad } \iota.$$

Substituting this in (9a) we find

$$\frac{\varepsilon_o}{c^2}\frac{\partial^2 \mathbf{e}}{\partial t^2} - \Delta \mathbf{e} = -\frac{1}{c^2}\,\iota\,\frac{\partial^2 \mathbf{E}_o}{\partial t^2} + \frac{1}{\varepsilon_o}\,\mathrm{grad}\left\{\mathbf{E}_o\ \mathrm{grad}\ \iota\right\} = \mathbf{a}\ ; \tag{9b}$$

we have to consider the right hand side of this equation as a known vector which we denote by "**a**." We see that there exists between the field of opalescence **e** and the vector **a** a relation of the same form as between the vector potential and the electric flux. The well known solution is

$$\mathbf{e} = \frac{1}{4\pi}\int \frac{\{\mathbf{a}\}_{t_o - \frac{r}{V}}}{r}\,d\tau, \tag{12}$$

where r is the distance of $d\tau$ from the point at which we consider **e**, and $V = c/\sqrt{\varepsilon_o}$ is the velocity of propagation of the light waves. The volume integral is to be extended over the whole space in which the exciting field $\mathbf{E}_o$ is different from zero. If we extend it only over a part of this space, we obtain only a fraction of the field of opalescence, namely that part of it which is due to the action of the exciting light wave in the part of space considered.

We propose now the problem of finding that part of the field of opalescence which is produced by an exciting monochromatic light wave inside of a cube

$$o < x < l,$$
$$o < y < l,$$
$$o < z < l.$$

The dimensions l of this cube shall be small compared to the dimensions L of the cube introduced before.

The exciting plane wave shall be given by

$$\mathbf{E}_o = \mathbf{A}\cos 2\pi n\left(t - \frac{\mathbf{nr}}{V}\right) \tag{13}$$

where **n** is the unit vector perpendicular to the plane of the wave (with components α, β, γ) and **r** the radius vector with the initial point at the origin (components x, y, z). We consider a point on the X axis of our system of coördinates, whose distance D from the origin shall be, for the sake of simplicity, infinitely great in comparison with l. For such a point equation (12) takes the form:

$$\mathbf{e} = \frac{1}{4\pi D}\int \{\mathbf{a}\}_{t_1 + \frac{x}{V}}\,d\tau, \tag{12a}$$

because we have to put

$$t_o - \frac{r}{V} = t_o - \frac{D - x}{V}$$

and we use for abbreviation

$$t_o - \frac{D}{V} = t_1;$$

we can substitute for the factor $1/r$ in the integrand the constant factor $1/D$ which differs from it only infinitesimally.

We have now to calculate the integral appearing in (12a) over our cube of edge l, taking for **a** its expression in (9b). We make this calculation easier by introducing the following symbol. If φ is a scalar or a vector function of x, y, z and t, we put

$$\varphi\left(x, y, z, t_1+\frac{x}{V}\right)=\varphi^*$$

so that φ^* depends only on x, y and z. For a scalar we have immediately

$$\operatorname{grad} \varphi^* = (\operatorname{grad} \varphi)^* + \mathbf{i}\frac{1}{V}\left(\frac{\partial\varphi}{\partial t}\right)^*,$$

where $\mathbf{i}$ denotes the unit vector in the direction of the X axis and it follows from this that

$$\int(\operatorname{grad} \varphi)^* d\tau = \int\operatorname{grad} \varphi^*\, d\tau - \mathbf{i}\,\frac{1}{V}\int\left(\frac{\partial\varphi}{\partial t}\right)^* d\tau.$$

The first integral of the second term may be transformed through partial integration. If $\mathbf{N}$ denotes the outside unit normal vector to the surface limiting the volume over which we integrate, and ds the element of surface, then

$$\int\operatorname{grad} \varphi^* d\tau = \int\varphi^*\mathbf{N}ds.$$

We have therefore

$$\int(\operatorname{grad} \varphi)^* d\tau = \int\varphi^*\mathbf{N}ds - \mathbf{i}\frac{1}{V}\int\left(\frac{\partial\varphi}{\partial t}\right)^* d\tau. \tag{14}$$

If φ is a function of an undulatory character then the surface integral in the right hand side of our equation furnishes no contribution which is proportional to the volume of integration; we can say more: it furnishes no contribution which has to be taken into account. In this case, therefore, an integral of the form

$$\int(\operatorname{grad} \varphi)^* d\tau$$

can furnish a contribution only to the X component.

If we form now the two integrals which arise when we substitute the expression for $\mathbf{a}$ given by equation (9b) in the integral

$$\int\mathbf{a}^* d\tau$$

appearing in (12a), we see that the second of these integrals has just the form of the left hand side of (14), φ being in this case $\mathbf{E}_o \operatorname{grad} \iota$. Since this is actually a function of undulatory character and, moreover, grad ι vanishes at the surface, the second integral can furnish, according to (14), an appreciable contribution only to the X component of $\mathbf{e}$. A more detailed calculation shows that this second integral just compensates the X component of the first integral. But we need not prove this because the vanishing of $\mathbf{e}_x$ is a consequence of the transversality of light. It follows, therefore, from (12a) and (9b) if we take into account what has just now been said

$$\left.\begin{aligned}\mathbf{e}_x &= 0,\\ \mathbf{e}_y &= -\frac{1}{4\pi Dc^2}\int\iota\left(\frac{\partial^2\mathbf{E}_{0y}}{\partial t^2}\right)^* d\tau\\ \mathbf{e}_z &= -\frac{1}{4\pi Dc^2}\int\iota\left(\frac{\partial^2\mathbf{E}_{0z}}{\partial t^2}\right)^* d\tau.\end{aligned}\right\} \tag{12b}$$

We shall now calculate $\mathbf{e}_y$ from the second of these equations; from (13) we have

$$\left(\frac{\partial^2 \mathbf{E}_{0y}}{\partial t^2}\right)^* = -\mathbf{A}_y (2\pi n)^2 \cos 2\pi n \left(t_1 + \frac{x}{V} - \frac{\alpha x + \beta y + \gamma z}{V}\right);$$

for ι we use the expression which follows from (8) and (5). Interchanging the signs of summation and integration we have

$$\mathbf{e}_y = \frac{\mathbf{A}_y (2\pi n)^2}{4\pi D c^2} \frac{\partial \varepsilon}{\partial \rho} \sum_\rho \sum_\sigma \sum_\tau B_{\rho\sigma\tau} \iiint \cos 2\pi n \left(t_1 + \frac{(1-\alpha)x - \beta y - \gamma z}{V}\right)$$

$$. \cos\left(2\pi\rho \frac{x}{2L}\right) . \cos\left(2\pi\sigma \frac{y}{2L}\right) . \cos\left(2\pi\tau \frac{z}{2L}\right) dx\, dy\, dz,$$

the integral being extended over the volume of the cube with the edge of length l. The volume integral is of the form

$$J_{\rho\sigma\tau} = \iiint \cos\left(2\pi n t_1 + \lambda x + \mu y + \nu z\right) \cos \lambda' x \cos \mu' y \cos \nu' z\, dx\, dy\, dz$$

and we have to consider λ, μ, ν, λ', μ', ν' as very large numbers.* If we perform the integration indicated and neglect terms which contain in the denominator one or more of the very large quantities $(\lambda + \lambda')$, etc., we have to put

$$J_{\rho\sigma\tau} = \left(\frac{1}{2}\right)^3 l^3 \frac{\sin(\lambda - \lambda')\frac{l}{2}}{\frac{(\lambda - \lambda')l}{2}} \cdot \frac{\sin(\mu - \mu')\frac{l}{2}}{\frac{(\mu - \mu')l}{2}} \cdot \frac{\sin(\nu - \nu')\frac{l}{2}}{\frac{(\nu - \nu')l}{2}}$$

$$. \cos\left(2\pi n t_1 + \frac{(\lambda - \lambda')l}{2} + \frac{(\mu - \mu')l}{2} + \frac{(\nu - \nu')l}{2}\right).$$

We see that $J_{\rho\sigma\tau}$ differs from zero appreciably only for such values of ρ, σ, τ for which the differences $(\lambda - \lambda')$, etc., are not very large. We note that we have put

$$\left.\begin{aligned} \lambda &= \quad 2\pi n \frac{1-\alpha}{V}, & \lambda' &= \frac{\pi\rho}{L}, \\ \mu &= -2\pi n \frac{\beta}{V}, & \mu' &= \frac{\pi\sigma}{L}, \\ \nu &= -2\pi n \frac{\gamma}{V}, & \nu' &= \frac{\pi\tau}{L}. \end{aligned}\right\} \qquad (15a)$$

We have now, if we use the abbreviation

$$\frac{\mathbf{A}_y (2\pi n)^2}{4\pi D c^2} \frac{\partial \varepsilon}{\partial \rho} = A,$$

$$\mathbf{e}_y = A \sum_\rho \sum_\sigma \sum_\tau B_{\rho\sigma\tau} J_{\rho\sigma\tau} \qquad (12c)$$

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* In the calculation which follows λ, μ, ν are taken to be *positive*. If this is not the case, then one or more signs in (15) have to be changed. But the final result is the same.

Together with (15) and (15a) this equation gives the value of the field of opalescence for every given moment $t_0 = t_1 + D/V$ at the point $x = D$, $y = z = 0$. We are especially interested in the average intensity of the light of opalescence, the average being taken both with respect to time and with respect to the variations in density which produce the opalescence. We may take as a measure of the average intensity the average value of $\mathbf{e}^2 = \mathbf{e}_y{}^2 + \mathbf{e}_z{}^2$. We have

$$\mathbf{e}_y{}^2 = A^2 \sum_{\rho}\sum_{\sigma}\sum_{\tau}\sum_{\rho'}\sum_{\sigma'}\sum_{\tau'} B_{\rho\sigma\tau} B_{\rho'\sigma'\tau'} J_{\rho\sigma\tau} J_{\rho'\sigma'\tau'}$$

the sum being extended to all combinations of the indices ρ, σ, τ, ρ', σ', τ'—always for the same value of t_1. We form now the average of this quantity with respect to the different distributions of density. We see from (15), that the quantities $J_{\rho\sigma\tau}$ do not depend on the distribution of densities; neither does the quantity A. We have therefore

$$\overline{\mathbf{e}_y{}^2} = A^2 \Sigma\Sigma\Sigma\Sigma\Sigma\Sigma \overline{B_{\rho\sigma\tau} B_{\rho'\sigma'\tau'}} J_{\rho\sigma\tau} J_{\rho'\sigma'\tau'},$$

if we denote the average value of a quantity by a bar over the corresponding symbol.

But since, according to § 3, the quantities B follow (independently of one another) the Gaussian law of errors (at least as far as our approximation goes) we must have, except for the cases when $\rho = \rho'$, $\sigma = \sigma'$, *and* $\tau = \tau'$,

$$\overline{B_{\rho\sigma\tau} B_{\rho'\sigma'\tau'}} = 0.$$

The expression for $\overline{\mathbf{e}_y{}^2}$ reduces therefore to

$$\overline{\mathbf{e}_y{}^2} = A^2 \Sigma\Sigma\Sigma \overline{B^2{}_{\rho\sigma\tau}} J^2{}_{\rho\sigma\tau}$$

This is, however, not as yet the required average. We have to take also the average with respect to *time*. Time appears only in the last factor of the expression (15) for $J_{\rho\sigma\tau}$. If we consider that the time average of this factor is ½ and introduce the abbreviations

$$\left.\begin{aligned} \frac{(\lambda - \lambda')l}{2} &= \xi, \\ \frac{(\mu - \mu')l}{2} &= \eta, \\ \frac{(\nu - \nu')l}{2} &= \zeta \end{aligned}\right\} \qquad (16)$$

we obtain for the final average $\overline{\mathbf{e}_y{}^2}$ the expression

$$\overline{\mathbf{e}_y{}^2} = \tfrac{1}{2} A^2 . \left(\frac{l}{2}\right)^6 \Sigma\Sigma\Sigma \overline{B^2{}_{\rho\sigma\tau}} \frac{\sin^2\xi}{\xi^2} \frac{\sin^2\eta}{\eta^2} \frac{\sin^2\zeta}{\zeta^2}.$$

According to (7) $\overline{B^2{}_{\rho\sigma\tau}}$ is independent of $\rho\sigma\tau$: we therefore can put it before the summation signs. Further, the difference between two values of ξ which belong to consecutive values of ρ is, according to (16) and (15a), $\frac{\pi}{2}\frac{l}{L}$ and this is an infinitesimal quantity. It is, therefore, possible to transform the triple sum into a triple integral. From the remark just made we see that the interval $\Delta\xi$ between two consecutive values of ξ satisfies the relation

$$\Delta\xi \,.\, \frac{2}{\pi}\,\frac{L}{\rho} = 1$$

so that

$$\Sigma\Sigma\Sigma\, \frac{\sin^2\xi}{\xi^2}\,\frac{\sin^2\eta}{\eta^2}\,\frac{\sin^2\zeta}{\zeta^2} = \left(\frac{2}{\pi}\,\frac{L}{l}\right)^3 \Sigma\Sigma\Sigma\, \frac{\sin^2\xi}{\xi^2}\,\frac{\sin^2\eta}{\eta^2}\,\frac{\sin^2\zeta}{\zeta^2}\,\Delta\xi\Delta\eta\Delta\zeta,$$

and the last sum may be simply written as a triple integral. We conclude from (16) and (15a) that we may take $-\infty$ and $+\infty$ as the limits of these integrals; the whole sum equals, therefore, a product of three integrals each of which has the value π. If finally, we use equation (7), and substitute for A its expression, we find for $\overline{\mathbf{e}_y^2}$

$$\overline{\mathbf{e}_y^2} = \frac{RT_o}{N}\,\frac{\left(\frac{\partial\varepsilon}{\partial\rho}\right)^2}{v^3\,\frac{\partial^2\psi}{\partial v^2}}\left(\frac{2\pi n}{c}\right)^4 \frac{l^3}{(4\pi D)^2}\,\frac{\mathbf{A}_y^2}{2},$$

or, if we use throughout the specific volume and substitute the wave length λ for c/n,

$$\overline{\mathbf{e}_y^2} = \frac{RT_o}{N}\,\frac{v\left(\frac{\partial\varepsilon}{\partial v}\right)^2}{\frac{\partial^2\psi}{\partial v^2}}\left(\frac{2\pi}{\lambda}\right)^4 \frac{\Phi}{(4\pi D)^2}\,\frac{\mathbf{A}_y^2}{2}. \qquad (17)$$

Here Φ denotes the volume (the shape of this volume is of no importance) in which the amount of opalescence which we consider, is produced by the passing radiation. An analogous formula holds for the z component while the x component of $\mathbf{e}$ is zero. We see that the intensity and the state of polarization of the light of opalescence which is emitted in a given direction is determined by the projection of the electric vector of the exciting radiation on the normal plane to the ray of opalescence, and does not depend on the direction of propagation of the exciting radiation.* If we denote the intensity of the exciting light by J_e, that of the light of opalescence at a distance D in a definite direction from the point where the excitation takes place, by J_o, the angle between the electric vector of the exciting light and the normal plane to the ray of opalescence by φ, we have, according to (17),

$$\frac{J_o}{J_e} = \frac{RT_o}{N}\,\frac{v\left(\frac{\partial\varepsilon}{\partial v}\right)^2}{\frac{\partial^2\psi}{\partial v^2}}\left(\frac{2\pi}{\lambda}\right)^4 \frac{\Phi}{(4\pi D)^2}\cos^2\varphi. \qquad (17a)$$

We calculate now also the apparent absorption which is due to opalescence by integrating the light of opalescence over all directions. We obtain

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* It is not surprising that our light of opalescence has this property in common with the light of opalescence due to suspended bodies which are small compared to the wave length of light. In both cases we have irregular deviations from homogeneity of the substance through which the radiation passes and these deviations vary rapidly from place to place.

$$\alpha = \frac{1}{6\pi}\frac{RT_0}{N}\frac{v\left(\frac{\partial \varepsilon}{\partial v}\right)^2}{\frac{\partial^2 \psi}{\partial v^2}}\left(\frac{2\pi}{\lambda}\right)^4, \tag{18}$$

where α is the absorption constant, so that if the light passes a stratum of thickness δ the factor of attenuation is $e^{-\alpha\delta}$.

It is significant that the principal result of our study given by formula (17a) permits us to determine exactly the constant N, *i.e.*, the absolute magnitude of molecules. In what follows we shall apply this result to the special case of a homogeneous substance as well as to a binary mixture of liquids in the vicinity of the critical state.

§ 5. Homogeneous Substance.

In the case of a homogeneous substance we have to put

$$\psi = -\int p\,dv$$

and therefore

$$\frac{\partial^2 \psi}{\partial v^2} = -\frac{\partial p}{\partial v}.$$

We have, further, according to the relation of *Clausius-Mosotti-Lorentz*,

$$\frac{\varepsilon - 1}{\varepsilon + 2}v = \text{const.},$$

and therefore

$$\left(\frac{\partial \varepsilon}{\partial v}\right)^2 = \frac{(\varepsilon - 1)^2(\varepsilon + 2)^2}{9v^2}.$$

If we substitute these values in (17a) we obtain

$$\frac{J_0}{J_e} = \frac{RT_0}{N}\frac{(\varepsilon - 1)^2(\varepsilon + 2)^2}{9v\left(-\frac{\partial p}{\partial v}\right)}\left(\frac{2\pi}{\lambda}\right)^4\frac{\Phi}{(4\pi D)^2}\cos^2\varphi. \tag{17b}$$

The meaning of different letters in this formula which gives the ratio between the light of opalescence and the exciting light, if the former is measured at a distance D from the volume Φ which is primarily subjected to radiation, is the following:

R = the gas constant,
T = the absolute temperature,
N = the number of molecules in a gram molecule,
ε = the square of the refractive index for the wave length λ,
v = the specific volume,
$\frac{\partial p}{\delta v}$ = the isothermal derivative of the pressure with respect to the volume,
φ = the angle between the electric field vector of the exciting wave and the normal plane to the ray of opalescence considered.

The circumstance that $\partial p/\partial v$ is the derivative taken isothermally, and not adiabatically, is connected with the fact that, among all the states which belong to a given distribution of densities, the state of equal temperature for a given total energy, is the state of largest entropy and therefore of greatest statistical probability.

If the substance, with which we deal, is an ideal gas, we may put $\varepsilon + 2$ approximately equal to 3. We obtain for this case

$$\frac{J_o}{J_e} = \frac{RT_o}{N} \frac{(\varepsilon - 1)^2}{p} \left(\frac{2\pi}{\lambda}\right)^4 \frac{\Phi}{(4\pi D)^2} \cos^2 \varphi \qquad (17c)$$

Calculation shows that this formula might very well furnish an explanation for the existence of a predominantly blue light emitted by the ocean of air when a radiation passes through it.* It is remarkable that our theory makes no *direct* use of the assumption of a discontinuous distribution of matter.

§ 6. Mixture of Liquids.

According to its derivation, equation (17a) holds also for mixtures of liquids if we put

v = specific volume of a unit mass of the first component.

ψ = work which it is necessary to apply in order to bring a unit mass of the first component, by a reversible process at a constant temperature from the specific volume of temperature equilibrium to a certain other specific volume.

It is possible to express the quantity ψ through observable quantities if the vapor which is coexistent with the mixture of liquids may be considered as an ideal gas and the mixture as incompressible. In this case we find ψ with the aid of the following elementary considerations.

We denote by k the mass of the second component which is admixed to a unit mass of the first component. We may consider then k as a measure of the composition of the mixture, the total mass of which is $1 + k$. This mixture includes a vapor phase; let p'' be the partial pressure and v'' the specific volume of the second component in the vapor phase. Let us assume that the system is enclosed in a vessel, a part of a wall of which is semipermeable so that the second component (but not the first) may be made to pass through it in both directions in the state of gas. Assume, further, that we have another vessel of relatively infinite dimensions, which contains a relatively infinite amount of the mixture of the composition (characterized by k_o) for which we want to calculate the opalescence. Let the second vessel also contain vapor in a space with a semipermeable wall. Let us denote the corresponding values of the partial pressure and specific volume for the second component by p_o'' and v_o''. Let the temperature inside of each vessel be T_o. We calculate the work which it is necessary to apply in order to increase by the amount dk the measure of concentration k in the first vessel through the transport, in a reversible way, of the mass dk of the second component from the second vessel. This work is composed of the following three parts:

$-\frac{dk}{M''} p_o'' v_o''$ (Work done in removing gas from second vessel.)

$\frac{dk}{M''} RT_o lg \frac{p''}{p_o''}$ (Isothermal compression to conform with partial pressure in first vessel.)

$+\frac{dk}{M''} p'' v''$ (Work done in introducing gas into first vessel.)

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* Equation (17c) may also be obtained by summing up the radiations emitted by the single gas molecules and assuming that their distribution is entirely irregular. (Compare Rayleigh, *Phil. Mag.*, 47, p. 375, 1899, and Papers, 4, p. 400.)

We neglect here the volume of the liquid as compared to the volume of the gas. M'' is the molecular weight of the second component in vapor phase. Since the first and the third term compensate each other, according to the law of *Mariotte,* we obtain

$$d\psi = \frac{RT_o}{M''}\, dk\ lg\frac{p''}{p_o''}.$$

The function ψ is thus directly calculable from concentrations and partial pressures. We have now to find $\partial\psi^2/\partial v^2$ for the state which we denote by the index "$_o$." We have

$$lg\left(\frac{p''}{p_o''}\right) = lg\left(1+\frac{p''-p_o''}{p_o''}\right) = lg(1+\pi) = \pi - \frac{\pi^2}{2}\ldots,$$

where π is the relative change of pressure of the second component in comparison with the original state. It follows from the last two equations that

$$\frac{\partial\psi}{\partial v} = \frac{RT_o}{M''}\frac{\pi - \frac{\pi^2}{2}\cdots}{\frac{\partial v}{\partial k}}.$$

Differentiating once more with respect to v and considering that

$$\frac{\partial}{\partial v} = \frac{\frac{\partial}{\partial k}}{\frac{\partial v}{\partial k}}$$

we obtain, on making $\pi = 0$ in the result,

$$\left(\frac{\partial^2\psi}{\partial v^2}\right)_o = \frac{RT_o}{M''}\frac{\frac{\partial\pi}{\partial k}}{\left(\frac{\partial v}{\partial k}\right)^2} = \frac{RT_o}{M''}\frac{\frac{1}{p''}\frac{\partial p''}{\partial k}}{\left(\frac{\partial v}{\partial k}\right)^2}.$$

If we take this into account and notice that

$$\frac{\partial\varepsilon}{\partial v} = \frac{\frac{\partial\varepsilon}{\partial k}}{\frac{\partial v}{\partial k}},$$

then the formula (17a) becomes

$$\frac{J_o}{J_e} = \frac{M''}{N}\frac{v\left(\frac{\partial\varepsilon}{\partial k}\right)^2}{\frac{\partial\,(lgp'')}{\partial k}}\left(\frac{2\pi}{\lambda}\right)^4\frac{\Phi}{(4\pi D)^2}\cos^2\varphi. \qquad (17d)$$

This formula, which contains only quantities which can be determined by experiment, determines the properties of opalescence of binary mixtures of liquids, inasmuch as their saturated vapors can be treated as ideal gases, completely with the exception of a small region in the close vicinity of the critical point. It would seem, however, that the possibility of a quantitative determination in this region is excluded in any event because of strong absorption of light and its great dependence on temperature. We repeat here the meaning of the symbols which appear in the last formula and which have not been explained after formula (17b).

M'' is the molecular weight of the second component in vapor phase,
v the volume of the mixture in which a unity of mass of the first component is contained,
k the mass of the second component which corresponds to a unity of mass of the first component,
p'' the pressure of vapor of the second component.

It might seem strange that in (17d) the two components play different rôles; but we notice that there exists a known thermodynamic relation

$$\frac{1}{M''}\frac{dp''}{p''}=-\frac{1}{M'}\cdot\frac{1}{k}\frac{dp'}{p'}.$$

We can conclude from this that it makes no difference which component we consider as the first and which as the second.

A quantitative experimental investigation into the phenomena dealt with here would be of great interest: it certainly would be worth while to know whether *Boltzmann's* principle actually predicts correctly the phenomena considered and, on the other hand, we could obtain through such investigations exact values for the number N.

I desire to express my thanks to Dr. Ludvik Silberstein and to Prof. Paul L. Saurel for aid in reading proof of this paper, so splendidly translated by Prof. Rainich.

The next paper deals with further aspects of light scattering, and some remarks on the significance of opalescence are given on p. 17 *et seq.* J. A.

The Scattering of Light in One-Phase Systems

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Historical Review

The fundamental theory of Light-Scattering in one-phase systems—often called molecular scattering—was written many years before the first laboratory observation of such scattering was made. The reason for this inversion of the usual sequence is that the theory of scattering in one-phase systems was patterned after the theory of scattering developed in relation to experimental work done on true colloidal solutions. Rayleigh[1] developed a theory which satisfactorily accounted for the observed scattering by transparent colloidal particles; while Garnett[2] and Mie[3] extended the theory to include the case of scattering by metal sols.

On the basis of the kinetic theory of matter, any pure gas, liquid or solid should scatter light for exactly the same reason as does a true colloidal solution in which there are particles small compared to the wave-length of light. We have only to let our colloidal particle surrounded by its dispersing phase become a molecule surrounded by space. Although the molecular scattering of light would then appear to be a necessary corollary of any molecular hypothesis, a long controversy has raged as to the existence of light-scattering in dust-free media.

In 1899 Rayleigh[4] showed that according to his theory the light scattered by dust-free air was sufficient to account for the observed intensity, color and polarization of the light of the sky. Abbott and Fowle,[5] and King[6] from data on the attenuation by the atmosphere of solar radiation, after making allowance for the effect of dust, and on the assumption that the extinction is all due to scattering, calculated the Avogadro number to be 6.23×10^{23}; the agreement of which with the accepted value lent considerable support to Rayleigh's theory of the blue color of the sky.

In 1913 the author, working in Professor F. B. Kenrick's laboratory on the removal of dust from liquids, came to the conclusion[7] that the scattering observed in liquids freed of dust by various methods was a property of the liquids themselves. Apart from the early observations on critical opalescence, this is the first statement based on direct experimental evidence that any dust-free medium scatters light. In 1915 Cabannes observed in the laboratory the scattering of light by dust-free air and other gases,[8] and soon afterwards Smoluchowski[9] and R. J. Strutt[10] working independently confirmed Cabannes' results.

Following upon these researches a great deal of experimental work has been done on scattering in gaseous and liquid media, until it is now well established that all dust-free gases and liquids—and probably solids—scatter sufficient light to permit of visual and photographic study.

LIGHT SCATTERING BY GASES

Lord Rayleigh[4] formulated the relations for scattering by a nearly transparent medium, consisting of particles much smaller than the wave-length of light, of spherical optical symmetry, and distributed at random. His theory leads to the following relation:

$$\frac{Ir^2}{EV} = \frac{\pi^2(\mu^2 - 1)^2}{2n\lambda^4}(1 + \cos^2\theta) \tag{1}$$

where I is the illumination of a plane normal to the scattered beam, at a distance r from the medium of volume V causing the scattering, and in a direction making an angle θ with the direction of propagation of the exciting beam.

E is the illumination of a plane normal to the exciting beam, supposed parallel and unpolarized.

n is the number of scattering particles per unit volume.

λ is the wave length of light, and μ is the index of refraction of the scattering medium.

This scattered light will be completely polarized in the plane containing the incident and scattered rays if $\theta = \frac{\pi}{2}$, and for any value of θ the ratio of the weak to the strong polarized component as seen, for example, through a properly oriented double image prism is $\cos^2\theta$. The two limiting hypotheses on the basis of which the above relations are deduced are (a) that the scattering particles are optically isotropic, and (b) that they are distributed entirely at random. The latter condition, according to the kinetic theory, is fulfilled by the molecules of a gas which obeys Boyle's law.

EXPERIMENTAL WORK ON GASES

A. The Polarization of Scattered Light.

R. J. Strutt,[11] Cabannes[12] and Gans[13] using a photographic method have studied the state of polarization of the light scattered by a number of gases in a direction at right angles to that of the incident beam. The gases were freed of suspended matter by Tyndall's method of filtration through cotton wool.[14] The results for a number of gases are given in Table I, column 4, where the depolarization factor is defined as the ratio of the intensity of the weak to that of the strong polarized component of the scattered light, the exciting light being unpolarized.

TABLE I

Gas	Relative Intensity of Scattered Light (Air 1) Observed	Calculated from (2)	Depolarization Factor
Air	1.00	1.00	0.040
Oxygen	0.90	0.86	0.054
CO_2	2.62	2.65	0.095
Nitrogen	0.95	1.03	0.028
Hydrogen	0.23	0.22	0.017
Argon	0.79	0.85	0.004
Helium	—	—	0.00
Benzene	—	—	0.06
CS_2	—	—	0.12
Ether	26.80	27.90	0.017

It is evident that for no gas except possibly the monatomic gases argon and helium is the scattered light completely polarized. The hypothesis that the molecules are isotropic must then be modified. The more complete investigation, which includes the case of scattering by particles of any shape, shows that formula (1) must be replaced by

$$\frac{Ir^2}{EV} = \frac{\pi^2(\mu^2 - 1)^2}{2n\lambda^4} \times \frac{6(1+\rho)}{6-7\rho} \times \left(\frac{1+\cos^2\theta+\rho\sin^2\theta}{1+\rho}\right)_{*}^{(15)1} \qquad (2)$$

The factor $\frac{6(1+\rho)}{6-7\rho}$, due to Cabannes, is called the Cabannes' correction factor.

Rayleigh[16] in one of his last papers indicated how the depolarization factor could be evaluated in terms of certain parameters of the molecule related to the "shape" of the molecule. For a gas the limiting possible values of ρ are 0 and 0.5; the former being the value of ρ for molecules of spherical symmetry, while the latter would result from molecules in which the vibration could occur in only one direction. If we make the arbitrary assumption that the molecule is an ellipsoid of revolution, so that we can express its shape in terms of two variables, then the ratio of the two axes of the ellipsoid could be determined from measurements of ρ. Some interesting calculations of this kind have been made by J. J. Thomson,[17] Gans[18] and Havelock.[19]

B. The Intensity of the Scattered Light.

For the same gas at different pressures and temperatures it is well established that the depolarization is constant and that the intensity of the scattering varies as the density, as would follow from Equation (1) since $\frac{(\mu^2-1)^2}{n}$ is proportional to the density. There is some contradictory evidence as to whether at high pressures where the gas departs appreciably from Boyle's law the same rule holds. Strutt[20] found that for carbon dioxide at pressures up to 60 atmospheres the intensity of scattering was proportional to the pressure. Ramanathan's[21] results are quite contradictory to this conclusion. Strutt says that his own apparatus leaked at high pressures and the balance of evidence points to a breakdown in Equation (1) for gases at high pressures.

For various gases at the same pressure and temperature the scattering should vary as $(\mu^2-1)^2\frac{1+\rho}{6-7\rho}$. The comparison of observed and calculated values of relative intensities in Table I shows this is true within the experimental error.

It is evident from (2) that a measurement of the ratio of scattered to exciting light leads very directly to a determination of n, the number of molecules of a gas per c.c. Cabannes has made this measurement with the greatest care, using argon gas. He deduces a value of the Avogadro number $(6.90 \pm 0.25) \times 10^{23}$. It would seem that this method of determining n is as accurate as other methods and that the theory on which it is based rests upon few and simple assumptions.

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* For derivation of this last factor see Bibliography 15.

LIGHT SCATTERED BY DENSE MEDIA

Rayleigh's formula for scattering, depending as it does on the assumption of random distribution of the molecules, could not be applicable to such media as liquids or highly compressed gases. Rayleigh himself says ". . . When the volume occupied by the molecules is no longer very small compared to the whole volume, the fact that two molecules cannot occupy the same space detracts from the random character of the distribution. . . ."

Smoluchowski [22] and Einstein [23] have investigated the scattering in such dense media using the theory of fluctuations of density due to the thermal motions of the molecules. By the use of Boltzmann's principle these fluctuations are evaluated in terms of the isothermal compressibility of the medium. Smoluchowski finds for the mean square of the fluctuation of density of a small volume φ of density d_0

$$(\overline{\Delta d})^2 = \frac{RT\beta_0 d_0^2}{N\varphi} \tag{3}$$

where β_0 is the isothermal compressibility; R is the gas constant $= 8.31 \times 10^7$; T is the absolute temperature; N is the Avogadro number $= 6.5 \times 10^{23}$. From the Lorentz-Mossotti relation $\frac{\mu^2 - 1}{\mu^2 + 2} = \text{constant} \times d$, the variations of refractive index resulting from these variations of density are found; and the light scattering is then calculated by a method not essentially different from Rayleigh's method, the final expression for the scattering being:

$$\frac{Ir^2}{EV} = \frac{\pi^2 RT\beta_0(\mu^2 - 1)^2(\mu^2 + 2)^2}{18N\lambda^4}(1 + \cos^2\theta). \tag{4}$$

Correcting this expression to allow for the observed imperfection of polarization of the scattered light we have corresponding to (2)

$$\frac{Ir^2}{EV} = \frac{\pi^2 RT\beta_0(\mu^2 - 1)^2(\mu^2 + 2)^2}{18N\lambda^4} \times \frac{6(1 + \rho)}{6 - 7\rho} \times \frac{1 + \cos^2\theta + \rho\sin^2\theta}{1 + \rho}. \tag{5}$$

L. V. King [24] makes two slight changes in (5). He substitutes the adiabatic for the isothermal compressibility and omits the factor $\frac{(\mu^2 + 2)^2}{9}$ from the formula.

It will be noted that (5) is much more general than (2) since: (i) for gases which obey Boyle's law, where $\beta_0 = \frac{1}{p}$, and $\mu^2 + 2 = \text{almost } 3$ (5) reduces to (2). (ii) It purports to hold true for all sorts of dense gases and liquids. (iii) It accounts for the remarkable opalescence of gases and liquids near the critical condition.

This formula too like (2) "enjoys the property of invariance with respect to details of molecular structure." Einstein goes so far as to say that ". . . our theory does not make *direct* use of the assumption of a discrete distribution of matter." It is, however, well to keep in mind that local fluctuations of density within a medium are a necessary consequence of the kinetic theory, while apart from it their hypothesis becomes purely arbitrary.

Scattering in Liquids

A. Experimental Method.

The study of scattering in liquids becomes possible only after all the dust has been removed. There are several methods of removing dust from liquids: Cataphoresis,[25] the dust being attracted to the electrodes when a potential difference is maintained between them. Envelopment,[25] the dust being carried down by gelatinous precipitates such as aluminium hydroxide. Ultrafiltration[26] through membranes such as collodion. But the method which has proven most convenient and most generally applicable is that of distillation in vacuo[27] without ebullition (Figure 1).

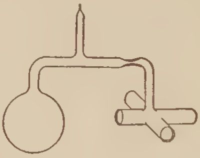

Fig. 1.

Any liquid which can be thus distilled without decomposition can very easily and in any quantity be freed of dust. The dust-free liquid is examined in the cross-shaped container, the exciting light entering and the scattered light being observed through sealed-in flat glass end-plates. It is very difficult to make these seals with soda or lead glasses but proved very easy when pyrex tubes and plates were used. The cross-shaped container was used here as it was also used in all experiments on scattering in gases, since it gives the best black background against which the faint scattered light may be observed.

B. The Polarization and Intensity of the Scattered Light.

Measurements of the polarization and the relative intensity of the light scattered by about twenty different liquids have been made by Martin and Lehrman[28] (Table II). Some of these measurements have been repeated by Raman[29] and Cabannes,[30] whose results are for the most part in good agreement with those listed in the table.

TABLE II

Liquid	Relative Intensity of Scattered Light (Benzene 1) Observed	Calculated	Depolarization Factor
Water	0.068	0.088	0.109
Methyl alc.	0.191	0.187	0.071
Ethyl alc.	0.200	0.223	0.078
n-propyl alc.	0.260	0.228	0.085
Isobutyl alc.	0.280	0.255	0.085
Isoamyl alc.	0.298	0.233	0.090
Ether	0.355	0.324	0.10
Benzene	1.00	1.00	0.485
Toluene	1.14	1.02	0.49
Xylene	1.26	1.12	0.52
Chlorobenzene	1.46	1.15	0.54
Carbon bisulph.	4.55	4.85	0.71
Chloronaphthalene	4.90	6.50	0.78

It is evident from a comparison of the depolarization factors listed in Tables I and II that all substances polarize the scattered light much less completely in the liquid than in the gaseous state. It is noteworthy also that, where data for both liquid and gas are at hand, the substance which has a relatively high depolarization factor in the gaseous state has also a high depolarization factor in the liquid state.

L. V. King has compared the observed relative intensities with those calculated from his modification of Einstein's formula. Table II shows that the agreement is fairly satisfactory. The relative intensities calculated from Einstein's formula (5) are of course not greatly different, but King's modification seems to fit the observations somewhat better.

Cabannes [30] has sought a theoretical explanation of the very large values of ρ observed for liquids. In the liquid state the electric field within the molecule will be distorted by the neighboring molecules. The effect of this external field may be expressed in terms of the diameter of the molecule. Cabannes' investigation leads to the following relation between ρ_L and ρ_V —the observed depolarization factors for the liquid and vapor states—and δ, the diameter of the molecule,

$$\frac{(\rho_L - \rho_V)(3 - 4\rho_V)}{(7\rho_L + 3)(1 + 2\rho_V)} = \frac{9R^2}{20\pi} \cdot \frac{d}{M} \cdot \frac{1}{N\delta^3} \tag{6}$$

where R = the molecular refraction; d the density; M the molecular weight of the liquid; and N the Avogadro number.

Substituting the experimental values for ρ_L and ρ_V Cabannes finds for the minimum diameter for the molecule of ether 2.90×10^{-8} cm. of benzene and carbon bisulphide 2.2×10^{-8} cm., results which are in very happy agreement with values of δ deduced from other considerations.

An interesting deduction from (6) is that, if we assume that ρ_V is independent of λ (there is need of more definite experimental proof that this is true), then ρ_L must change with λ since R changes with λ. It follows from (6) indeed that the polarization of the scattered light should be more complete, the longer the wave-length of the light; and that for different liquids, those liquids with high dispersive power should show the greatest variation of the depolarization factor with λ. Cabannes has studied the variation of ρ_L with λ for liquid carbon bisulphide and for benzene and obtains results in agreement with (6). Raman [31] finds that for all liquids which he studied the polarization was slightly more complete for red than for blue light; but that water, which has the smallest dispersion, shows the greatest variation of ρ with λ, and that toluene with a relatively high dispersion shows a constant value of ρ. There is need of a further study of a number of liquids with monochromatic light to settle this question.

C. Scattering by Liquids at High Temperatures.

According to Einstein's theory (see Equation 5) the intensity of scattering in liquids should vary greatly with temperature since T, μ and β_0 are all functions of temperature. The compressibility in particular increases rapidly with temperature for all liquids and approaches infinity at the critical temperature. Several liquids have been studied at temperatures up to or approaching their critical temperatures—ether and benzene by Ramanathan,[32] n-pentane by Vankateswaran,[33] and benzene and heptane by Martin and Lehrman.[34] In all cases the liquids were rendered dust-free by distillation in vacuo, and heated in strong glass bulbs under the pressures of their vapors. As appears from the example given below, which is typical of all the liquids studied, the intensity of the scattering increases with temperature and becomes very great near the critical temperature, falling off again rapidly above the critical temperature. This intense scattering near the critical condition is the well-known critical opalescence of carbon dioxide and other gases.*

TABLE III

Scattering by Liquid Ether (Ramanathan)

Temperature t°	$\frac{\text{Scattering at } t^\circ}{\text{Scattering at } 35^\circ}$		Depolarization Factor
	Observed	Calculated from (5)	Observed
33	1.00	1.00	0.080
61	1.23	1.34	0.080
80	1.85	1.66	0.070
104	2.30	2.13 at 100°	0.075
125	3.00	—	—
145	4.90	8.20 at 150°	0.030
170	12.00	14.10 at 175°	0.017 at 165°
179	22.00	—	—
185	38.00	27.20	—
190.5	82.00	73.00 at 190°	0.013 at 189°
193.6 (crit.)	750.00	(3.164 g. ether in 13.98 c.c.)	0.012
194	378.00	290.00 at 195°	0.012
198	126.00	—	0.012
202	64.00	65.00	0.012
212.5	27.00	30.00	0.012
217	21.00	26.00	0.012

The polarization becomes more complete as the critical temperature is approached and at the critical temperature becomes almost but not quite complete. In the case of benzene the value of the depolarization factor near the critical temperature is much smaller than for the gas at room temperature. Equation (5) seems to fit the facts rather well as is shown in the second and third columns of the table. In the case of benzene and hexane it is impossible to compare the results with the theory because of the lack of data on the compressibility of the liquids at high temperatures.

Raman [31] has attempted to explain theoretically the great decrease in the depolarization factor with rising temperature. He considers the scattered light as arising from two causes. (i) A part due to fluctuations of density which when observed at right angles to the incident beam is completely polarized and the intensity of which is given by Einstein's Equation (4). (ii) A part which Born [35] calls the orientation scattering and which is due to the random orientation of the anisotropic molecules. This part is to a first approximation completely unpolarized and its intensity is proportional to the density even when we pass from the gaseous to the liquid state.

This theory is successful in accounting for the falling off of the depolarization factor with rising temperature since the polarized part (i) increases rapidly with temperature while the unpolarized part (ii) decreases with rising temperature. It may be pointed out, however, that the theory outlined above is in conflict with Cabannes' theory for scattering in liquids,[30] since according to the former a liquid composed of isotropic molecules scatters completely polarized light, while according to the latter this is not the case.

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* Practically considered, this amounts to the formation of a colloidal dispersion of the liquid in the gas—a true isocolloid. J. A.

D. Scattering by Liquid Solutions.

Measurements have been made of the scattering by several pairs of two-component liquid solutions [28] and the results of some of the measurements are shown graphically in Fig. 2.

The curves show that the relative intensity of the scattered light is always somewhat greater than that calculated on the assumption that the scattering is an additive property for the two components. Liquids which polarize the scattered light very far from completely show on dilution much more complete polarization. The dotted lines in A and B of Figure 2 are the intensity and polarization curves calculated on the assumption that each of the components scatters light in exactly the same way as regards polarization and intensity as does the pure liquid.

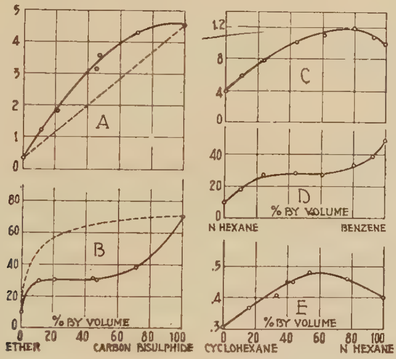

FIG. 2.

Solutions of Carbon Bisulphide and Ether. A. Relative Scattering.
B. Per cent Polarization.
Solutions of Benzene and Normal Hexane. C. Relative Scattering.
D. Per cent Polarization.
Solutions of Normal Hexane and Cyclohexane. E. Relative Scattering.

Einstein [23] has extended his theory of local fluctuations of density in a pure liquid to include the case of fluctuations of concentration in a liquid solution. He finds for the composition scattering:

$$\frac{Ir^2}{EV} = \frac{\pi^2}{2}\,\frac{M''v}{N\lambda^4}\,\frac{\left(\frac{\partial\mu^2}{\partial k}\right)^2}{\frac{\partial(\log p'')}{\partial k}}(1+\cos^2\theta)^* \qquad (7)$$

where M'' is the molecular weight of the second component in the vapor phase; v is the volume of solution in which is contained unit weight of the first component; k is the weight of the second component which is dissolved in unit weight of the first component; p'' is the partial vapor pressure of the second component.

To this composition scattering must be added the density scattering due to local fluctuations of density in the liquid given by (4) where μ and β_0 are now the values of the refractive index and the compressibility of the solution in question.

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* Einstein's theory is quite general, so that it may be easily extended to include also scattering in solutions of non-volatile solutes. For this case data on the osmotic pressure of the solution could be used in place of data on partial vapour pressure.

A comparison of the observed intensities with those calculated from the theory outlined above is difficult, because of the lack of data on the partial vapor pressures and compressibilities of the liquids. Raman and Ramanathan consider[36] that the theory is in at least qualitative agreement with the observations. A recent study by Rav[37] on solutions of carbon bisulphide and acetone, the partial vapor pressures of which are known, shows that as regards both polarization and intensity the experimental results are in excellent agreement with the Einstein theory for solutions.

E. Critical Opalescence.

It has long been known that whenever we approach a true critical condition at which two phases in equilibrium become identical, there is visible as much as several degrees above and below the critical temperature a remarkably intense opalescence.*

Einstein really had in mind this phenomenon of Critical Opalescence when he developed his theory which has proven to be much more general than even he had anticipated. The probability of local fluctuations of composition in a solution (or of local fluctuations of density in a pure liquid or gas) is greater as we approach the critical condition since there the decrease of entropy involved in the fluctuations of composition becomes less (Boltzmann-Gibbs relation). This is evident also in expression (7) where the factor $\frac{\partial(\log \rho'')}{\partial k}$ becomes very small as we approach the critical temperature since there the composition of the vapor phase does not change with the composition of the liquid phase.

Experimental studies of critical opalescence of the gas-liquid critical condition have been made by Travers and Usher,[38] Kamerlingh-Onnes and Keesom[39] and recently by Andant.[40] These researches confirm quantitatively the Einstein theory (see Equation 4) as regards the variation of the intensity of opalescence with the wave-length of the exciting light and the temperature of the liquid, except at temperatures extremely close to the critical temperature where obviously the formula could not apply since it indicates an infinite scattering at the critical temperature. From measurements of the ratio of incident to scattered radiation for ethylene near its critical temperature, Kamerlingh-Onnes and Keesom find for the Avogadro number the value 7.5×10^{23}.

So intense is the opalescence in the case of binary liquid mixtures near the critical temperature and ternary mixtures near the Plait Point[41] that many workers have found it difficult to determine just when the true critical point is attained.

Fürth[42] has studied spectrophotometrically the intensity of the critical opalescence of phenol-water mixtures as a function of the wave-length and polarization of the exciting light and the concentration and temperature of the mixture. His results are in remarkably good agreement with Equation (4). Zernike[43] has made a similar study of mixtures of diisobutyl nitrobenzene and pentamethylene methyleneiodide. He finds for the Avogadro number value between 6.2 and 6.5×10^{23}. Ornstein and Zernike[44] also have extended Einstein's theory to make it applicable in the immediate neighborhood of the critical temperature.

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* See paper by A. Einstein, this volume. J. A.

Scattering in Solids.

We have very little data concerning molecular scattering in solids. Certainly under careful observation the scattered light may be observed in the clearest crystals. Raman has measured the scattering in a quartz crystal and in some samples of glass.[45] He has also attributed the blue light coming from within the ice of a glacier to molecular scattering. No evidence has been given, however, in any case that these solids are free of inclusions, and until we have some evidence to this effect it seems futile to make measurements.

From the standpoint of the diffraction theory a perfectly regular arrangement of molecules within a crystal would result in no scattering. The thermal agitation of the molecules would, however, result in some departure from this regular arrangement, and might be expected to result in a feeble scattering.

Selective or Resonance Scattering.

In all the cases of scattering discussed above light of every frequency is scattered, the intensity varying simply as λ^{-4}. R. W. Wood [46] and Rayleigh [47] have, however, observed that mercury vapor scatters an enormous amount of light when excited by the mercury emission line 2536 Å. The scattered light is but very slightly polarized. The region of the spectrum in which this resonance scattering is found is extremely narrow, being only 0.01 Å in width. The addition of very small amounts of air or helium changes greatly the intensity and polarization of this resonance scattering. There is not yet sufficient data at hand to form a basis for an adequate theory of resonance scattering. It seems simplest to postulate that where this intense selective scattering is found, the period of vibration of the exciting light corresponds with a natural period of vibration of the molecule so that resonance results. It is not clear why this resonance scattering should be observed only in case of one of the mercury emission lines. There is need of a study of scattering in both gases and liquids in the neighborhood of absorption bands. The theory of resonance scattering must be related to the general theory of absorption.

The Blue Color of the Sea.

The cause of the blue color of the sea has been the subject of considerable discussion.[48] There are at least three factors, each of which independently would give the sea a blue color:

(1) Light from the sky reflected from the surface. The amount of this reflected light varies with the angle of observation. Looking straight down into the sea only about two per cent of the light of the sky is reflected.

(2) Water exerts a selective absorption on light of the longer visible wavelengths, so that a white object, seen through a long column of water, appears distinctly blue. Thus any light returning from below the surface of the sea would have a blue color.

(3) Of the light entering the sea, supposed of unlimited depth, all which is not absorbed and converted to heat must be either reflected back by relatively large particles or scattered back by very small suspended particles or by the water itself. This light scattered back by the small particles or the water would be sky-blue in color.

There is a lack of definite data on the relative importance of these factors in different parts of the sea. Raman claims [49] that molecular scattering contributes very largely to the blue of the sea. If this be the case sea water must contain extremely little suspended matter. Shoulejkin[50] considers that scattering is quite important compared to sky-reflection but attributes the scattering in the Black Sea to suspended impurities in the water rather than to the water itself. Judging from conditions, this third factor seems to be the one most responsible for the color of the Blue Grotto at Capri.

Ramanathan[51] has observed too that water taken from places in the Indian Ocean where the sea appeared green showed on examination in the laboratory a definite greenish fluorescence which is attributed to organic matter in the water.

It will be evident from this chapter that a considerable amount of experimental work has already been done in the few years since light-scattering in one-phase systems was first observed. Theoretical interest in the whole subject has been stimulated by reason of the intimate relationship which exists between the theory of scattering and the general theory of light propagation in material media. The study of light-scattering seems also to be a rather direct method of attack on the problem of the "Constitution of Matter" which is so much to the fore at the present time in both Physics and Chemistry.

The theory will no doubt be modified as more experimental data are obtained, but it is difficult to see how need may arise for any fundamental changes in the particular theory of Rayleigh or the more general theory of Smoluchowski and Einstein. Any theory of scattering at present conceivable must postulate some sort of discontinuity of matter. Smoluchowski's theory of density fluctuations has been the key to the solution of the problem of scattering in all sorts of media. This is not in reality a new theory but rather a most ingenious method of evaluating the fluctuations of density which result from the thermal agitation of the molecules postulated in the classical kinetic theory.

Smoluchowski's work on the application of the principles of statistical mechanics to kinetic theory problems has already provided excellent theories of Brownian movements as well as of Light-Scattering. His theory of density fluctuations * is not generally found in books on kinetic theory or colloid chemistry but it deserves to be better known and more widely used.

Scattering in Anisotropic Liquids.

Many liquids under certain special conditions are optically anisotropic and exhibit the property of double-refraction. The majority of these liquids are double-refracting only when subjected to the action of an electric or magnetic field. A smaller number, however, between certain sharp temperature limits are spontaneously double-refracting: these are the so-called liquid crystals.

The theory advanced to explain both the above types of anisotropy rests on the hypothesis that the molecules of these liquids are very asymmetric, so that under the influence of an electric or magnetic field, or in the case of liquid crystals without the action of any external force the molecules to some extent attain a common orientation.

Since the same hypothesis of asymmetric molecules is used to explain the considerable imperfection in polarization of the light scattered by dust-free liquids and gases, it follows that those liquids which show strong double-refraction either spontaneously or in an electric field should show also the least complete polarization of the scattered light.

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* For review and bibliography see Fürth, Schwankungserscheinungen in der Physik. Sammlung Vieweg (1920).

A. Liquids Which Are Double-Refracting in an Electric or Magnetic Field.

Gans * has recently deduced a quantitative relation between the state of polarization of the scattered light and the Kerr constant of electrical double-refraction for liquids. This relation has been tested out for some fifteen liquids † and it is found that the relation holds well for twelve of the liquids. For chloroform, methyl alcohol and water Gans' equation is not in agreement with experiment. Gans makes it clear, however, that his relation will hold ". . . only for fluids whose molecules have no permanent electric moment in the Debye sense." The three liquids mentioned above are just those which, from considerations of their other physical properties, such as the variation of their dielectric constants with temperature, might be expected to have a large permanent electric moment. It is to be hoped that someone will extend the theory so as to include these special liquids.

B. "Liquid Crystals."

Para-azoxyanisol ‡ melts at 116° to a turbid liquid which under the polarizing microscope resembles a disordered mass of small uniaxial crystals. In this condition its scattering could not be studied on account of its turbidity but at 135° it passes quite sharply to the ordinary liquid condition. The dust was removed from the liquid by filtration through a Mandler diatomaceous earth filter. The depolarization factor for this liquid at 145° in white light was 0.85.

Now for a liquid composed of molecules in which vibration can occur in only one direction—the extreme of asymmetry—the calculated value of the depolarization factor is 0.86. The experimental result 0.85 is then in accord with the hypothesis of needle-shaped molecules in this type of liquid crystals.

Surface-Scattering in Liquids.

Smoluchowski in his paper (1908) on critical opalescence points out that, when light is reflected at a liquid surface, we should expect besides the regularly reflected ray a slight diffuse scattering of light at the surface. This surface scattering would arise from fluctuations at the surface just as internal scattering would arise from fluctuations in the body of the liquid. It is evident, too, that as we approach a critical condition at which the compositions of the two phases forming the surface approach each other the surface scattering should greatly increase.

Mandelstam § has given the quantitative theory of this surface-scattering in which he shows how it depends on the surface tension, the refractive index, the wave length and the angles of incidence and of observation. The relation was tested out by Mandelstam for the case of light incident on the boundary between the two layers of a mixture of methyl alcohol and carbon bisulphide near the critical solution temperature.

Raman ¶ has published a series of papers in which he gives the results of measurements of the surface-scattering of a large number of dust-free liquids at room temperature. He has also studied the surface opalescence of liquid carbon dioxide near the critical temperature and of some binary liquid mixtures near the critical solution temperature. Raman has also observed the surface scattering of mercury. The theory in the case of mercury —given recently by Gans *—differs somewhat from that for a transparent liquid. In all cases of surface scattering the intensity varies as λ^{-2} rather than λ^{-4} as is the case for internal scattering.

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* *Zeit. Physik,* **17**, 353 (1923).

† *Jour. Phys. Chem.,* **28**, 1284 (1924).

‡ *Roy. Soc. Canada,* III, **19**, 36 (1925)

§ *Annalen der Physik,* **41**, 609 (1913).

¶ *Annalen der Physik,* **74**, 231 (1924).

It would seem to be possible to draw from work of this kind important conclusions as to the nature of thin films on liquid surfaces. Raman has made a few observations on the effect of minute amounts of oleic acid on the surface scattering of water. "The observations of surface-opalescence thus seem clearly to confirm the existence at one stage, as contemplated by Hardy, Langmuir and Adam, of a continuous film of the oleic acid of extreme tenuity whose surface tension is lower than that of water and whose light-scattering power is correspondingly larger."

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* *Proc. Roy. Soc.*, A **108**, 561; A **109**, 150, 272 (1925).

The Action of Light Upon Suspensions

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Quincke[1] has already remarked that certain colloids behave themselves differently when the vessels in which they are contained are exposed to the light: some have a tendency to precipitate upon the wall exposed to the light, others, on the contrary, upon the wall lighted the least. It appears then that there is both a positive and negative phototropy.

Intuitively, it may be thought that light can act directly upon cohesion and modify its value. It is probable, indeed, that it is the peripheral electrons of the atoms which determine cohesion (or affinity, which is perhaps not essentially different from it). Now it is these electrons which produce the phenomenon of absorption or of emission. There is nothing illogical, therefore, in supposing that a radiation of a frequency in the neighborhood of visible light, modifies the stationary system of one or several of these cohesion (or affinity) determining electrons. In the case of affinity, photochemical reactions constitute an argument in favor of this hypothesis. If light may act in the case of chemical phenomena, it may probably also intervene in the case of a physical phenomenon such as cohesion and modify the intensity of the forces put in play. Moreover, it is probable that for the atomic scale, physical and chemical phenomena are differentiable with difficulty; they constitute simply two appearances of the same reality. In a very general paper, J. Perrin[2] has shown that perhaps it is light, in the broadest sense of the term, which produces chemical reactions. In extending his postulate, he has shown that one may also connect with it physical phenomena such as the changes of state (vaporization, crystallization, fusion), and in studying phosphorescence, he has finally formed the opinion that light intervenes in reactions inside the atom, where several stationary stable states are possible, by inducing the change of one of these states into another.

The action of light upon the equilibrium of disperse systems may be foreseen. The qualitative study of this action is relatively easy; it suffices to test out the precipitating or stabilizing action of radiation. But the quantitative study presents considerable difficulties. The choice of the suspension is very important. Furthermore, there have been few experiments along this line.

First Part. Action of Light Upon Suspensions of Sulfur[3]

1. Choice of Suspension.

In order to study easily the precipitation of a suspension, it is desirable that certain properties should vary considerably during the precipitation; it is necessary besides that this variation be not too rapid, so that the change of the properties considered may be made conveniently determined. In both these respects suspensions of sulfur are particularly suitable.

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* Translated by Dr. E. P. Wightman (Eastman Kodak Co.).

When sulfur is precipitated from a solution of sodium thiosulphate by means of an acid, there is obtained a turbid liquid at first red by transmitted light, but which, according to the concentrations of the reagents employed, soon absorbs less of the short wave lengths, and when viewed by transmitted light is at first blue and finally violet. Then it sediments and the deposit of amorphous sulfur thus collected gradually crystallizes.

This change in optical properties is connected especially with the variation in size of the particles in suspension. It has been shown[4] indeed by systematic studies that at constant concentration the absorption of the turbid medium depends upon the size of the particles in suspension. Suspensions of mastic and of gamboge, consisting of particles of dimensions small compared to a wave length of incident light, diffract especially the short wave lengths; viewed by transmitted light such suspensions appear red. On the contrary, for the same particle concentration, suspensions of gamboge and mastic, consisting of spheres of diameter greater than a wave length of incident light, diffract preferentially the radiations of greater wave[*] length; such media transmit blue light. Independently of the possible influence of concentration, there is, then, every reason to suppose that the variation in the optical absorption of sulfur suspensions during their evolution is due principally to the variation in particle size. The important variation of the optical properties of sulfur in suspension make it, therefore, an excellent suspension for study, for the period of evolution may be extended even to several days, which is more than sufficient.

It is preferable to utilize sulfur obtained by a physical method. For with sulfur obtained by the chemical precipitation, light may act directly in the course of the chemical reaction. Suspensions of sulfur are easily obtained physically by utilizing the general process employed in obtaining suspensions of gamboge or of mastic.

2. Preparation.

A turbidity generally results on mixing three substances A, B, C, where A is very soluble in B and C, while B and C are insoluble in each other. For example:

B	A	C
Water	Alcohol	Ether
“	“	Chloroform
“	“	Toluene
“	“	Thymol
“	“	Phenolphthalein

In this same category appear also mixtures such as:

B	A	C
Water	Alcohol	Colophany
“	“	Mastic
“	“	Gamboge
“	“	Sulfur
“	Acetone	Sulfur

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[*] In this case the formula of Lord Rayleigh $\frac{I}{I_0} = e^{-\frac{B}{\lambda^4}}$ does not apply and may be replaced by the formula $\frac{I}{} = e^{-\frac{B}{\lambda^n}}$ (Boutaric, Thesis 1918), where n may be positive or negative (Cheneveau and Audubert, *Compt. rend.*, 168, 766 (1919).

Suspensions of sulfur, which is soluble in acetone and in alcohol, may be thus obtained.

It is difficult to prepare stable suspensions by precipitating with water a solution of sulfur in acetone or alcohol. According to the conditions of preparation (concentrations, temperature), the suspensions precipitate in a time which varies from several hours to several days.

In order to perform the experiments under nearly identical conditions, all the suspensions were prepared by precipitating a definite quantity of a 2.1 per cent solution of sulfur in acetone, by an equal quantity of distilled water. To obtain suspensions with different precipitation velocities, it suffices to introduce into the intergranular liquid variable quantities of electrolytes. ($BaCl_2$, $MgCl_2$, $NaCl$.) The velocity of precipitation is, in fact, an increasing function of the concentration of the electrolyte in the intergranular liquid and of the valence of the cation, at least for the three mentioned.*

3. Action of Temperature.

When a few drops of water are added to a solution of sulfur in alcohol or in acetone, there are formed at ordinary temperatures particles of sulfur which grow very rapidly. The white turbidity † produced quickly becomes blue and then violet to transmitted light as the particles grow; finally, all of the sulfur is precipitated at the bottom of the tube. If one adds to the supernatent liquid a few more drops of water, the same phenomenon is produced with less intensity and decreasing velocity, until the last traces of water added produce a suspension of very fine particles which diffract especially the shorter wave lengths, and appear blue by diffraction.

Summarizing, when dissolved sulfur is in excess, the particles formed are large; when the concentration of dissolved sulfur is small, the particles formed are small. If a suspension of sulfur thus obtained, either from an alcoholic or an acetone solution is heated to a temperature of 50 to 60°, the liquid clears, the precipitate partially redissolves while at the same time the sedimentation of part is accelerated. On cooling the suspension reforms. This phenomenon may also be produced by adding to an alcoholic solution of sulfur in the neighborhood of its boiling point, a few drops of water at a temperature in the neighborhood of 80°; whereupon there is obtained a precipitate of sulfur which disappears by simple agitation, but which reappears gradually as the temperature drops. This phenomenon is explained by the increase of solubility with temperature, and by the great increase of the velocity of precipitation of the particles already formed, because of the very great diminution in viscosity. Further, the temperature, by augmenting the velocity of agitation of the particles increases the number of encounters according to the mechanism mentioned above.

4. Residual Solubility.

One is thus led to think that when the suspension has just formed, the intergranular liquid still contains molecules of dissolved sulfur which may more slowly pass into suspension.

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* When one wishes to prepare a suspension of sulfur starting from an alcoholic solution, it is necessary to heat the alcohol gently in order to dissolve in it a sufficient quantity of sulfur. This process prevents the realization each time of identical conditions, the conditions of preparation (concentrations, temperature) being very badly defined. It is for this reason preferable to employ acetone solutions.

† The velocity of evolution is too rapid for the red phase to be observed.

This residual solubility is evidenced by the following experiments: By pressure filtration of a suspension of sulfur through a fine grained porous candle, there is obtained a clear liquid, all of the particles having been stopped by the filter; by again adding water to the filtrate, a very fine precipitate of sulfur may be obtained. In most cases, the suspension obtained by the second precipitation is very dilute, and the presence of a suspension of very fine particles is revealed only through the bluish diffraction produced by sending a very intense pencil of light through the suspension. The experiment is not only a delicate one, but the filtration may also be made very rapidly. One may also demonstrate the residual solubility of sulfur in the alcohol-water mixture by centrifuging energetically (9,000 revolutions per minute) a precipitate of sulfur obtained as previously indicated. The supernatent liquid is clear and gives with water a very fine precipitate. This procedure, however, has proved less satisfactory than the preceding, having given positive results in only two cases.

In conclusion, it is evident that mixtures of water-alcohol, water-acetone, may dissolve very small quantities of sulfur; and on the other hand that after the precipitation the intergranular liquid yet contains some sulfur in a dissolved state, which precipitates only very slowly.

Optical Properties[3]

5. Optical Absorption.

The optical properties of a suspension of sulfur are characteristic.

As the suspension is formed, the coefficient of transmission, $\frac{I}{I_0}$, decreases rapidly, passes through a minimum, and tends asymptotically towards unity in proportion to the sedimentation of the particles. The minimum depends upon the conditions of preparation of the suspension. The course of this variation is indicated in Fig. 1.

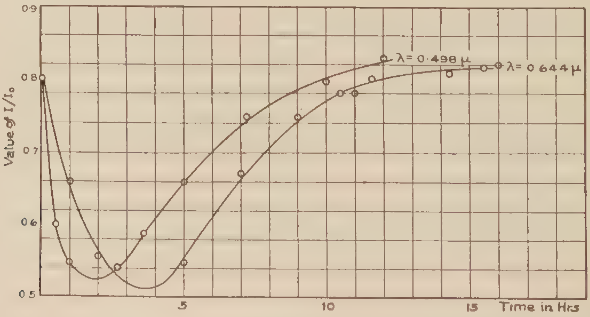

Fig. 1.—Coefficient of transmission of a suspension of sulfur.

6. Dispersion by Internal Diffusion.

As has been indicated above, the dispersive properties of sulfur suspensions vary considerably during the evolution of the suspension, since at the start, it is the shorter wave lengths which are for the most part dispersed while towards the end, before the complete sedimentation of the grains, it is, on the contrary, the rays of greater wave lengths. If the absorption is represented by the formula of Lord Rayleigh[5] generalized[6] for turbid media having particles larger than the wave length of the incident light, we have

$$\frac{I}{I_o} = e^{-\frac{A}{\lambda n}}$$

in which $\frac{I}{I_o}$ is the ratio of the intensity of the transmitted light to that of the incident light, A is a function of the concentration and of the diameter, and λ is the wave-length of the incident radiation. The exponent n of λ, represents the dispersive property of the medium. When n is > 0 the medium absorbs mostly the radiations of lesser wave-lengths—it transmits red; when n is equal to zero it absorbs equally all the radiations—in this case it transmits white when it is illuminated by a pencil of white light; on the other hand, when n is < 0 it is mostly the longer wave-lengths which are absorbed—by transmitted light, the suspension appears blue. For suspensions containing very small particles, n may be in the neighborhood of $+4$ (sky blue), for those containing larger particles n may be[7] in the neighborhood of -2.

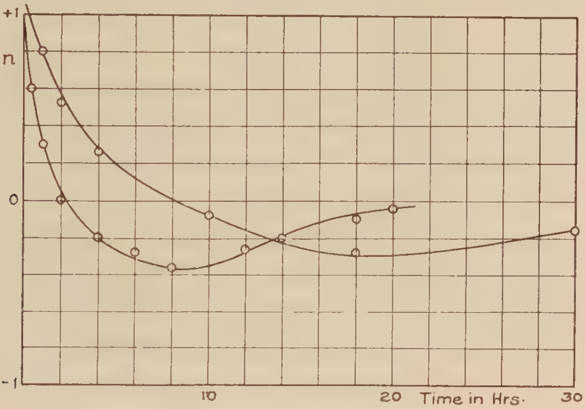

FIG. 2.—Variation of n with time.

The relative variation of n during the evolution of the suspension is then considerable and each modification in the process of evolution can be noted by determining the variation of n. The path of the curve $n = f(t)$ is indicated in Fig. 2.

It is seen that n decreases to a certain minimum, and then tends towards 0. The minimum is produced in general at the moment when sedimentation begins. It is therefore of no interest to consider the part of the curve following the minimum. Considering the descending part only, it is seen immediately that the form of the function $n = f(t)$, may be obtained. Indeed, by calling n_0 the initial value of n, and representing as ordinates the logarithms of the difference $(n_0 - n)$, and as abscissas the logarithms of the times, we obtained experimentally a straight line

$$\log (n_0 - n) = \text{Const.} + \log (t),$$

which gives

$$n_0 - n = K \,.\, t^{\beta};$$

as will be seen later, β is a coefficient independent of the conditions of preparation, while K, on the contrary, varies with the conditions.

The determinations of $(n_0 - n)$ reduces itself, then, to a simple formula, and the comparison of the resulting differences is facilitated.

The action of radiations is manifested as follows: the spectrum may be divided into two principal groups, radiations of short and radiations of long wave length. The former diminish the stability of the suspension by increasing the velocity of evolution; on the contrary, radiations of long wave length increase the stability of the suspension by diminishing the velocity of evolution. Between these two groups lie radiations in the neighborhood of yellow, without influence on the velocity of precipitation.

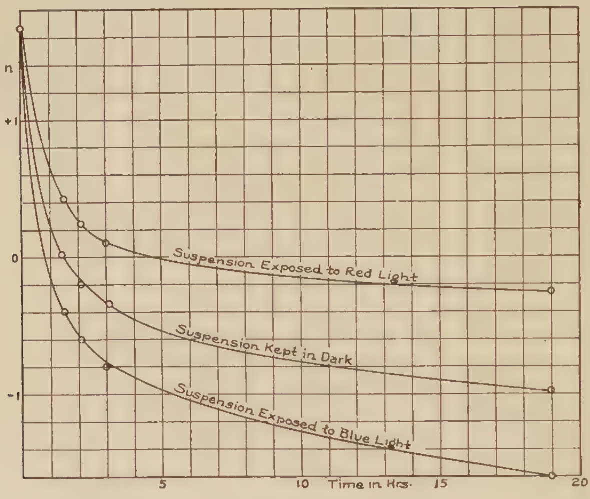

Fig. 3.—Variation of n with color.

TABLE I

Values of n (at 15°)

Time in Hours and Minutes	Dark	Radiations Red 0.7 μ to 0.6 μ	Yellow	Green 0.58 μ to 0.478 μ	Blue 0.7 μ to 0.65 μ and 0.478 μ to 0.450 μ
0	+1.77	+1.77	+1.77	+1.77	+1.77
1	+0.86	+1.03	+0.97	+0.79	+0.70
2	+0.76	+0.86	+0.77	+0.60	+0.50
4	+0.52	+0.60	+0.53	+0.22	+0.26
18	+0.00	+0.10	+0.02	−0.12	−0.24
0	+1.84	+1.84	+1.84	+1.84	+1.84
1	+0.10	+0.14		+0.00	−0.05
2	−0.16	−0.11		−0.16	−0.22
4	−0.51	−0.44		−0.60	−0.62
18	−0.90	−0.80		−1.04	−1.08
0	+1.66	+1.66	+1.66		+1.66
1:25	+0.02	+0.33	+0.12		−0.40
2: 5	−0.20	+0.24	−0.17		−0.60
3: 5	−0.34	+0.10	−0.30		−0.80
19: 5	−1.03	−0.27	−0.91		−1.60

The effect produced by the active radiations is intensified by removing radiations which do not produce any change, as is shown by Table I, which gives values of n for a series of experiments.

Fig. 3, which refers to this table, shows clearly the course of the variation of n as a function of time, and the change of this variation with exposure of the suspension to radiations of different wave length.

By representing as ordinates the logarithms of $n_0 - n$, where n_0 is the initial value of n, and as abscissas the logarithms of the time, it is seen from Fig. 4 that there is obtained for the values in the preceding table, straight lines, all of which have the same slope.

$$\log (n_0 - n) = A + \beta \log t.$$

β is independent of the manner in which the suspension has been obtained and of the conditions under which it is placed. Whatever may be the concentrations of the reagents when the chemical method is employed, or whatever may be the quantity of sulfur dissolved in the acetone or in the alcohol when one proceeds by the solution method, or whatever may be the dimensions of the grains formed and their number, there are always obtained parallel or approximately parallel lines. It is further remarkable to observe that β is independent of the wave length of the radiation to which the suspension is subjected. It seems then, that this coefficient depends only upon the nature of the suspension.

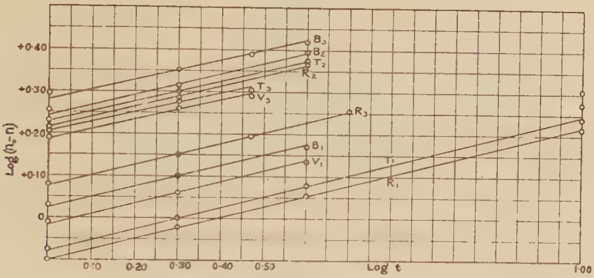

FIG. 4.—Log $(n_0 - n)$ plotted against log t.

T = suspension kept in dark.
R = suspension exposed to red light.
B = suspension exposed to blue light.
V = suspension exposed to violet light.
1, 2, 3 refer to the three different experiments of Table I.

It should be remarked that points corresponding to a too great duration of evolution, do not coincide well with the preceding law. This result, however, does not nullify the exactness of the form

$$\log (n_0 - n) = A + \beta \log t$$

It merely means that sedimentation has commenced. In this case then n has passed its minimum value, and diminishes while tending asymptotically towards zero. The points out of line correspond to that part of the curve $n = f(t)$ which is found after the minimum. It is then legitimate to represent $(n_0 - n)$ as a function of time; prior to the sedimentation by an equation of the form $n_0 - n = Kt^{\beta}$ in which β is a constant depending solely upon the nature of the particles of the suspension. By expressing the time in hours, the value of β is in the neighborhood of 0.26.

The constant K depends upon the conditions of formation and also upon the conditions in which the suspension is placed. The greater the velocity of evolution the higher are its values. Besides, it varies with the wave length of the radiation to which the liquid is submitted—the values corresponding to the red radiations are smaller than those with blue radiations, the suspensions exposed to yellow give the same results as the checks. According to experiments made with filters, the inactive radiations lie between 0.580 μ and 0.600 μ.

A series of experiments has given, for example, the values in the following table.

TABLE II

VALUES OF K

Check	Red	Yellow	Green	Blue
0.80	0.70	0.80	0.98	1.07
1.74	1.70	1.77	1.84	1.89
1.64	1.23	1.54	—	2.06

It is seen from this that radiations of short wave length increase the velocity of the precipitation, this action increasing with the frequency; and that the radiations of long wave length diminish the velocity of precipitation, this action varying inversely as the frequency.

MICROSCOPICAL STUDY

7. Variation of Diameter of the Particles.

On examining microscopically a suspension of sulfur particles, obtained by the methods indicated, we see that on the average the grains are nearly spherical. It is, besides, remarkable that most of the particles have about the same diameter. If the evolution is followed microscopically, it is seen that the diameter of the spherules increase with time, at first rapidly, then more and more slowly; finally the grains cease growing, but they agglutinate by twos, and as flocks form sedimentation takes place.

On studying the law of growth of the grains as a function of time, there is found a very simple exponential formula of the form

$$d - d_{t=0} = A(1 - e^{-bt})$$

which when t is small, reduces to the form $d = d_0 + bt$. At the outset, it is very easily found that the particles increase linearly as a function of time. This regular variation of the dimensions of the granules in the suspension may be explained if we keep in mind what the mechanism of the precipitation must be. Let us examine what should be produced when we dilute with water a solution of sulfur and acetone. The solubility of the sulfur in the mixture water-acetone is extremely slight, a great number of the primary molecules dissolved in the acetone agglomerate and form the suspension while a smaller fraction remains in the dissolved state in the intergranular liquid.

It has already been seen how this view may be considered established by experiment. The molecules, which at the moment of the formation of the suspension remain in solution, do not take long to precipitate upon the surface of the particles. This aggregation conserves the spherical form of the grains.

Then when the dissolved sulfur has been thus almost entirely fixed, the evolution of the suspension continues, but then it is the grains which aggregate to form flocks.

The law of the variation of the diameter as a function of time may be deduced from intuitive considerations, by supposing that the velocity of formation of the suspension is proportional on the one hand to the surface of the particles, and on the other to the quantity of sulfur not precipitated. We have:

$$V = \frac{dx}{dt} = KS(a - x)$$

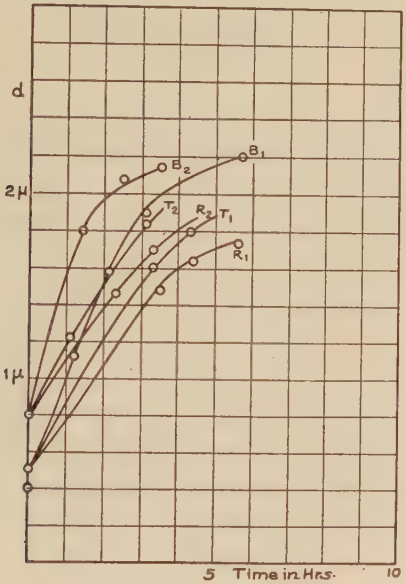

FIG. 5.

T = suspension kept in dark.
R = suspension exposed to red light.
B = suspension exposed to blue light.
1, 2 refer to different experiments.

in which x represents the mass of the suspension, S the surface of the granules, a the quantity of sulfur initially dissolved in the solvent. But $S = x^{2/3}$, from $\frac{dx}{dt} = Kx^{2/3}(a - x)$. The complete integration of this equation leads to a complicated function which expresses correctly the experimental results, but the utilization of which is not convenient. By supposing $(a - x)$ constant, we obtain on integration:

$$x^{1/3} = at + b$$

$$d = at + b$$

Initially the diameter varies linearly as a function of time, which is in accord with the experimental results.

A review of the figures resulting from the determination of the particle diameters, brings to light a curious result. Within the limit of experimental error, it can be shown that the angular coefficients of the tangents at the origin of the curves, representing the variation of the diameter as a function of the time, are approximately the same. This angular coefficient appears to be independent of the conditions of formation of the suspension and characterizes the nature of the suspension. In other words, the coefficient a of the preceding equation $d = at + b$, is independent of the conditions of formation of the suspension, and depends solely on the nature of the particles; b, on the contrary, is a function of the mode of formation. For example, a has been found approximately the same for suspensions obtained starting from either acetone or from alcoholic solutions, and whatever may have been in each case the relative concentrations of the constituents.

8. Action of the Light.

If we study the law of particle growth under varying wave length, we find that light of short wave lengths increases particle size more rapidly than long wave lengths.

Suspensions protected from all radiation present the same velocity of evolution as those exposed to the intermediary wave lengths (yellow), and this velocity lies between the first two. The angular coefficient of the tangent at the origin depends upon the wave length of the radiation to which the suspension is exposed, but not to the mode of formation of the suspension or the conditions under which it has been held. The curves in Fig. 5 show clearly these results.

The measurements of the growth of the spherules confirm the optical determination. One may now conclude that the radiations of short wave length increases the velocity of fixation of dissolved sulfur upon the surface of the granules, and that the longer wave lengths diminish it. It may finally be concluded that the diameter varies with the time, following an exponential form which it is always possible to confuse with a straight line during the first phase of the precipitation.

CONDUCTIVITY

9. Variation of the Conductivity of the Intergranular Liquid as a Function of Time.

If we consider a suspension containing N grains per cubic centimeter, with charge e, volume φ, mobility v, in an intergranular liquid of conductivity K', the conductivity K of this suspension is given by the formula:

$$K = N\psi + K' - K'N\varphi$$

in which ψ represents the conductivity due to one particle. It is impossible to define this term; the velocity of the ions constituting the ionic atmosphere of the grains is poorly defined; in other words, the actual charge of the latter is not well defined. Stokes' Law cannot apply, for it would mean that the two layers of the Helmholtz double layer would slide freely over each other, whereas the existence of an ionic atmosphere of appreciable thickness around the granule complicates the phenomena and it is probable that only part of the ions of this atmosphere is free *vis a vis* with those which are adsorbed by the particle surface itself.

Experiment leads to the following results:

(1) The conductivity of the suspension as a function of time remains practically constant.

(2) The conductivity of the intergranular liquid * decreases rapidly, passes through a very accentuated minimum and increases gradually, tending asymptotically towards a limiting value. The course of this variation is indicated in Fig. 6.

The existence of this minimum lies without doubt at the maximum through which the total surface of the particles passes when the fixation of the dissolver sulfur upon the nuclei becomes insignificant, and the agglutination of the grains among themselves is on the point of commencing. This maximum of the surface may indeed correspond to a maximum in adsorption of ions.

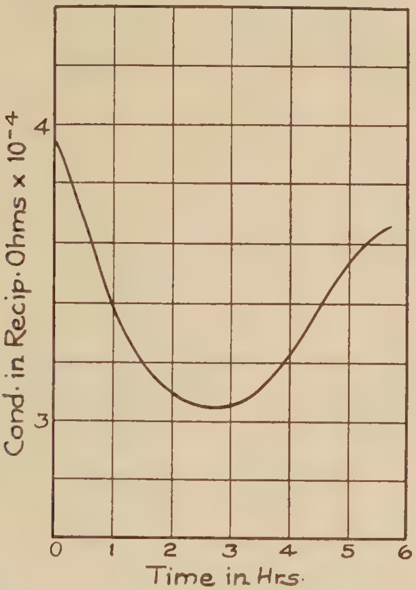

Fig. 6.

10. Action of Light upon the Conductivity of the Intergranular Liquid.

The study of this action leads to the following results. The tangent at the origin of the curves $K' = f(t)$ is steeper for suspensions exposed to radiations of short wave length than for those exposed to long wave lengths. The curves of the check suspensions lies between the two preceding. In other words the minimum is attained more rapidly in blue light than in darkness, and more rapidly in darkness than in red light. These results are shown in Fig. 7.

The effect produced by light may be explained thus: the radiations of short wave length augment the velocity with which the surface of the grains increases, the conductivity of intergranular liquid should therefore vary in-

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* The intergranular liquid may be separated from the granules by filtration under pressure through a fine-pored bougie. *Ann. de Phys.* (9), 18, July and August (1922).

versely to this growth; radiations of long wave-length produce the opposite effect.

STUDY OF MOBILITY

The mobility of the constituent particles of the suspension may also serve to show the action of light.

11. Mobility of the Granules of a Suspension of Sulfur in Evolution.

When we measure microscopically the variation in mobility as a function of time, we find a curve which presents a minimum, which is the more marked and the nearer to the origin the more concentrated the suspension, and, in consequence, the greater its velocity of evolution. For example, a sulfur suspension which undergoes its evolution in about 1½ to 2 hours presents a curve which shows the minimum at from 15 to 25 minutes. Besides, this suspension has a mobility which very rapidly attains a value greater than the initial mobility. On the other hand, with less concentrated suspensions, having a gradual evolution, the minimum mobility is reached only after a much longer time; for example, for a suspension whose evolution is produced in 20 hours, the mobility passes through its minimum after about three hours.

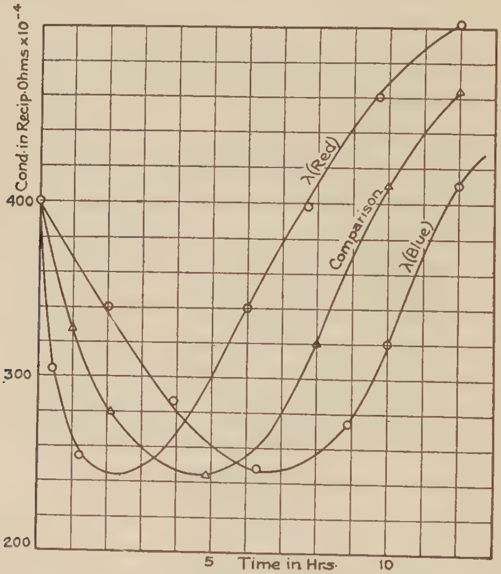

FIG. 7.

In certain cases, with very concentrated suspensions having very high velocity of evolution, no minimum has been observed; it is probable that this minimum is too fugitive to be noted. The time required for manipulation and microscopic examination is too great to permit our observing the minimum of mobility which probably occurs.

Fig. 8 reproduces some curves indicating the form of this variation.

The course of this curve again gives evidence that the evolution is probably the result of the superposition of two phenomena; (1) the fixation of the molecules of sulfur, predominating initially, (2) the agglomeration of the particles, which later plays the essential rôle.

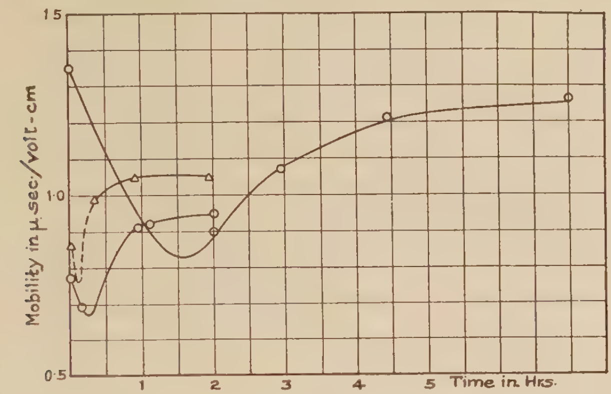

Fig. 8.

12. Action of Light upon the Mobility.

The preceding results relative to the influence of light upon the conductivity of intergranular liquid leads one to think that light may have an action upon the mobility of the particles, and that different rays have different effects. Experiment shows this to be the fact. This effect is quite similar to those described above for conductivity.

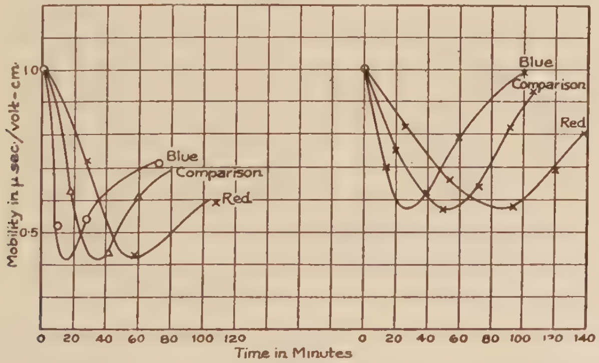

Fig. 9.

As the curves in Fig. 9 clearly show, different rays always act in the same way.

The curves corresponding to suspensions exposed to radiations of short wave lengths present a more rapid evolution than the curves corresponding to suspensions exposed to those of long wave length. The check suspensions are intermediate. It should be noted that the minima presented by suspensions exposed to different radiations show approximately equivalent intensities. It naturally suggests itself to compare the various curves, $I/I_0 = f(t)$, $K' = \varphi(t)$, $U = \psi(t)$, and to think that the minimum of I/I_0 as a function of time may correspond to the minimum of K' and of U. The verification of this is difficult because of the evolution of the suspension, of the time necessary to effectuate the operations and the measurements, and above all of the very great speed with which I/I_0 varies in the neighborhood of its minimum.

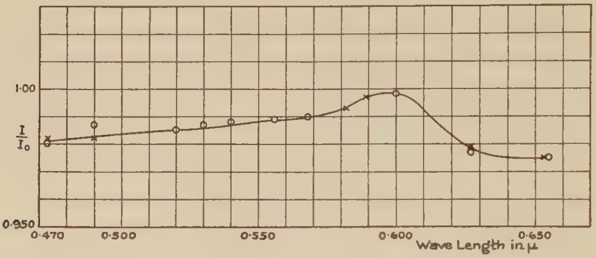

FIG. 10.

To repeat, the study of the different parameters characteristic of suspensions of sulfur: absorption, diameter and mobility of the particles, conductivity of the intergranular liquid, give evidence of the antagonistic action of the radiations of the visible spectrum. Only the yellow radiations have no action. Radiations of short wave length exhibit a contrary effect to those of long wave length; for the two groups of radiations the effect increases in proportion as the frequency deviates from the frequency of the inactive rays. The effect produced by short wave lengths is more intense as the frequency diminishes. This result very probably corresponds in the proportions in which the radiations are absorbed.[15]

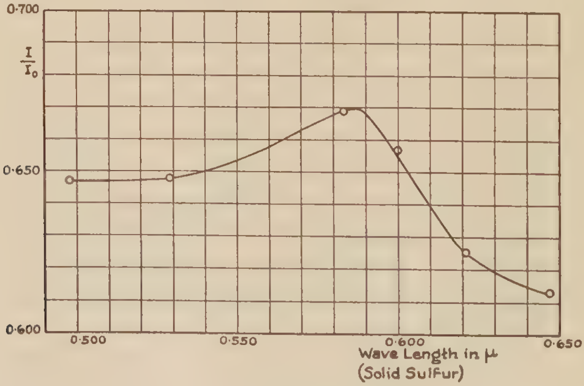

FIG. 11.

By placing before the slit of a spectroscope a pellicle of solid sulfur of 0.1 to 0.2 mm. thickness, obtained by cooling a drop of molten sulfur pressed between two plates of glass, it is found quantitatively that the red, blue and violet are particularly absorbed, but yellow radiations much less. Solutions of sulfur obtained with different solvents, benzene, chloroform, and in particular, carbon disulfide, are yellow and feebly absorb yellow rays.

The curves of Figs. 10 and 11, representing the variation of the coefficient of transmission with the wave length, have quite analogous courses. they show definitely that the radiations at the extremities of the visible spectrum are most absorbed. In other words, it appears, within the limits of experimental error, that the wave length corresponding to the minimum is the same for both solid sulfur and for sulfur dissolved in carbon disulfide, being in the neighborhood of $\lambda = 0.600\ \mu$.

These results lead by analogy to the view that the particles of sulfur in suspension may not behave differently with respect to the absorption of radiation, *i.e.*, the yellow radiations which are inactive during the process of the evolution of the suspension, correspond to a minimum of absorption.

APPLICATIONS

13. Study of the Transformation of Soluble Sulfur into Insoluble Sulfur.

For some time it has been known that under the influence of light, sulfur dissolved in certain solvents, carbon disulfide, benzene, carbon tetrachloride, is precipitated in the form of insoluble amorphous sulfur. This amorphous sulfur finally resumes the crystalline state. Berthelot [8] and Lallemand [9] who were the first to study this phenomenon, showed that the most active radiations were those of short wave length. Since their researches, this transformation has been the object of a great number of investigations; for instance, Rankin [10] found that the inverse transformation is produced spontaneously in the dark.

Wigand [11] has shown that ultra-violet rays which are the most active are correlatively very strongly absorbed. He has, in addition, observed that rise in temperature displaces the equilibrium by favoring the formation of soluble sulfur.

All of these researches, in short, contain the following essential points. On the one hand the radiations of short wave length provoke the transformation S (soluble) → S (insoluble); on the other hand, the inverse reaction S (insoluble) → S (soluble) is produced spontaneously in darkness and with an intensity increasing with the temperature.

All these facts have led S. E. Sheppard in his book on Photochemistry to represent this transformation by the following equation:

$$\text{S (soluble)} + \text{violet} \rightleftarrows \text{S (insoluble)} + \text{infra-red}.$$

This scheme comes entirely within the scope of the general equation of all photo-chemical transformation given by J. Perrin:

$$A + h\nu \rightleftarrows A' + h\nu'.$$

The results of the action of light on suspensions of sulfur, which may be attributed to influence of radiations upon the forces of cohesion, leads to the view that the transformation of soluble into insoluble amorphous sulfur is related to quite analogous phenomena. In this case, indeed, an increase in the forces of cohesion of dissolved sulfur brings about the association of dissolved molecules into granules, then into flocks which finally settle out.

Wigand[11] has studied in the ultra-microscope the phenomenon S (soluble) → S (insoluble). The process which he has observed is in all points identical with that of the evolution of a suspension of sulfur. The analogy may be pursued: the transformation S (soluble) → S (insoluble) is brought about especially by rays of high frequency; similarly the evolution of a suspension of sulfur is also very rapid with rays of short wave lengths. The action of temperature, though more complex, is also analogous: the reaction S (insoluble) → S (soluble) is favored by rise of temperature, which by increasing solubility, causes the disappearance of a turbidity already formed, providing its particles are not too large. To be sure, there is a slight difference between the two phenomena: the red radiations which are particularly active in retarding the velocity of evolution of a suspension of sulfur, have no action upon the transformation S (soluble) → S (insoluble). This difference may be attributed perhaps to the influence of the different solvents in which the transformation is produced. Carbon disulfide, indeed, is not transparent and its coefficient of absorption varies with the wave length.

It is seen from this comparison that the two phenomena are governed by the same cause. The transformation S (soluble) → S (insoluble) is the consequence of a modification of the forces of cohesion under the influence of light.

Study of the reaction $2H_2S + O_2 = 2H_2O + 2S$.—When a saturated solution of hydrogen sulfide is exposed to the air, the initial limpid liquid after a while becomes turbid. A suspension of sulfur is formed, which presents all the characteristics of the evolution of the suspensions of sulfur considered above: the grains, at first small, diffuse the short wave lengths, the liquid appears red by transmitted light; then its appearance becomes milky and after a time, sometimes rather long, it appears violet by transmitted light; finally it ends by sedimenting. It is reasonable to think that the light which modifies the velocity of evolution of a suspension of sulfur can accelerate or retard the oxidation of the hydrogen sulfide. Experiment shows that the same radiations tend to produce the same effects. Solutions exposed to blue radiations are much more rapidly precipitated than those which are left in the dark. The solutions exposed to the action of red radiations have a much slower velocity of evolution. The reaction is retarded, and in certain cases nearly stopped.*

The effect of the light upon this reaction has been studied by following the time-variation of the exponent *n* of the wave length, in the generalized formula of Lord Rayleigh.

TABLE III

Time	Solution Exposed to Red	Check	Solution Exposed to Blue
	Clearness	Clearness	Clearness
6 hrs.	+ 1.3	+ 0.9	+ 0.2
24 hrs.	+ 1.1	— 0.6	— 1.2

Perrin has shown in his generalized photochemical theory that the energy of all reactions is equal to a universal constant times the difference between ν and ν', which produces and destroys this reaction:

$$Q = H(\nu - \nu').$$

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* This justifies the long-established practice of pharmacists in using reddish brown bottles for sensitive solutions. Blue bottles should obviously be avoided in such cases, though they may be used for poison, etc. J. A.

Assuming that ν represents blue radiations since they accelerate the evolution, while ν' represents the red radiations which retard the formation of the suspension, and taking for ν and ν' the frequencies which correspond to the extremes of the visible spectrum, Q may be calculated. This gives in the neighborhood of 38,000 calories, while thermochemistry indicates in the neighborhood of 58,000. While this result is only approximate, it is none the less true that this very incomplete and much too simple interpretation leads to the right order of magnitude, where almost any result might have been obtained. It is necessary to point out that in spite of everything this application of pure photochemical theory in the case of sulfur is merely approximate, at first, because sulfur presents a continuous absorption curve, and furthermore, the real values of ν and ν' are probably different and without doubt beyond the visible spectrum. The calculation of $\nu - \nu'$ can be effected only by taking into account the absorption spectrum of sulfur in the infra-red and in the ultra-violet.

PART II. ACTION OF LIGHT UPON THE ADSORPTION OF IONS BY GAMBOGE AND MASTIC

We may now consider the action of radiation upon the adsorption of ions by suspensions.[3] The choice should be guided:

First, by stability.

Second, by the absorption of the constituent material of the particle for the rays of the visible spectrum.

For these two reasons the suspensions adopted were mastic and gamboge. They both consist of suspensions of small balls of constant diameter. Besides, the substances of which they are formed absorb especially the red and blue rays.

1. Spectrophotometry of Gamboge and of Mastic.

Gamboge and mastic are well adapted to spectrophotometric study. They give with solvents (alcohol, acetone, etc.) concentrated solutions of definite color. Besides, in the solid state, they are transparent as glass. The granules of mastic differ nevertheless slightly from those of gamboge. The former are rather less resistant and crush by pressure under the microscope cover glass, while the latter behave as veritable balls of glass and break into bits when submitted to the same operation.

It is possible to obtain solid transparent layers of these two substances by evaporating concentrated solutions in an oven in a tray having an optically plane bottom.

With gamboge the same result may be obtained by chilling some of the molten material upon a glass plate.

The author has studied spectrometrically the absorption of gamboge and of mastic. Absorption measurements have been carried out with various solutions of those substances, and with solid plates obtained as indicated above.

The results are as follows: Radiations in the neighborhood of yellow are less absorbed than radiations at the extremities of the visible spectrum.

Moreover, the wave length corresponding to this minimum of absorption, within the limits of error of the experiment, appear to be independent of the state of the substance when examined. The curves in Fig. 12 indicate these results for gamboge.

Curves of the coefficients of transmission of alcohol and acetone solutions are quite similar; those for gamboge in the solid state follow a slightly different course. However, they present a maximum like the others. Further, the wave length corresponding to the three maxima (about 0.600 μ) is probably the same.

These observations lead one to think then that the particles of a suspension of gamboge ought not to behave differently with regard to the absorption of light. Naturally, we must allow in this case for the loss of light due to optical phenomena: diffraction, reflection, diffusion, which occur with the grains of all suspensions.

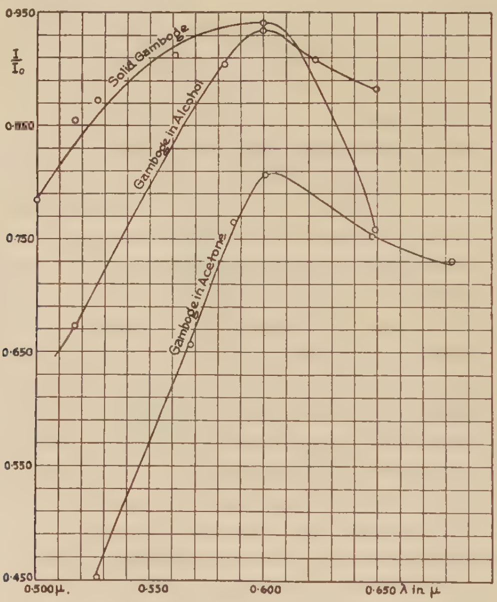

Fig. 12.

The spectrophotometric study of mastic leads to analogous results. The curves in Fig. 13 show for this substance also the existence or a maximum of absorption for radiations in the neighborhood of yellow. This maximum is probably in the neighborhood of 0.600 μ, but it is less easy to define the position than in the case of gamboge.

It is necessary to study the action of ions upon the electrophoresis of these grains.[16]

2. Influence of Various Ions H^+, La^{+++}, Al^{+++}, Ba^{++}, Mg^{++}, K^+, Na^+.

Suspensions of gamboge and of mastic consist of negative particles, whose charge is modified when positive ions are introduced into the liquid, the effect being more pronounced as the valence of the ion increases. When the decrease of the charge attains a certain point the stability of the suspension is destroyed, agglutination begins, the particles coalesce, and the flocks thus formed do not take long to settle. As we have seen, the decrease in the charge is not instantaneous. The establishment of equilibrium is definitely realized only at the end of a certain time, which may be as long as 30 minutes, being shorter with increasing concentration of the active ions.

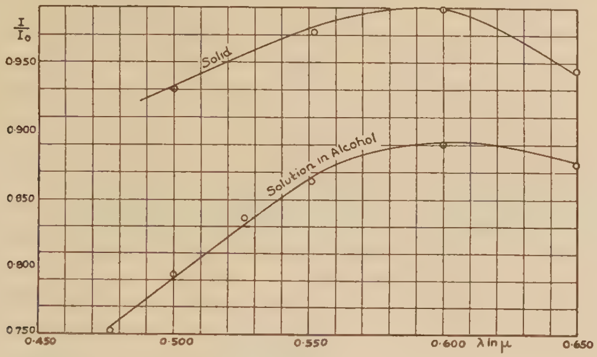

FIG. 13.

Before testing the influence of different radiations, the author studied the change in mobility of the particles by the addition of various electrolytes and as a function of the concentration of these electrolytes.

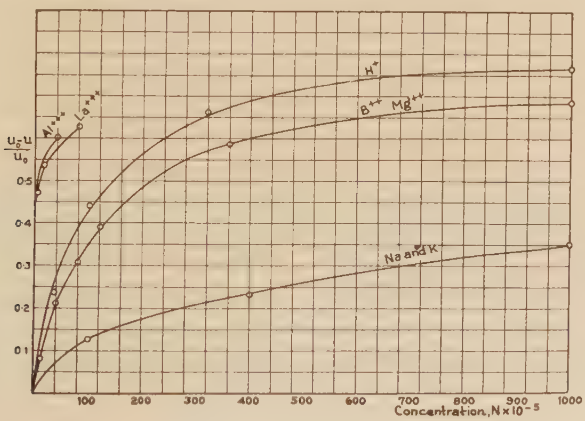

FIG. 14.

The adsorption of the different ions in various concentrations has been determined for H_2SO_4—HCl, for La^{+++}, Al^{+++}; for Ba^{++}, Mg^{++}; and for K^+ and Na^+; as the curves in Fig. 14 indicate the valence of the ion plays a large rôle. The curves have been obtained by taking as abscissas the values of different concentrations expressed in mols per liter, and as ordinates the values of the difference $\left(1 - \frac{U}{U_0}\right)$ in which U_0 represents the mobility before the addition of electrolyte. In restricting ourselves by graphing the variation of the difference $(U_0 - U)$, we obtain, for the same electrolyte, curves which do not always coincide. Indeed, although the suspensions are in each case obtained by diluting with a definite quantity of water the same quantity of pure solution, the values of U_0 show slight differences due perhaps to traces of impurities contained in the vessel. But in constructing the curves with the quantity $\frac{U_0 - U}{U_0}$, that is to say $\left(1 - \frac{U}{U_0}\right)$, we again find for the same electrolyte curves which at the same temperature coincide perfectly.

When the concentration increases markedly the decrease in mobility finally becomes quite negligible. The limit is generally attained for a concentration in the neighborhood of that at which agglutination begins.

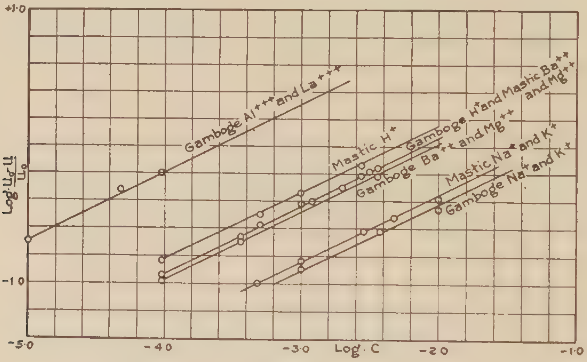

Fig. 15.

But if instead of choosing as abscissas the molecular concentration of the dissolved salt we choose the concentration of ions, taking into account the coefficient of ionization of the salt at each corresponding dilution, the mobility of the spherules increases constantly with the ion concentration as long as we keep below the agglutination point.

On studying these last curves plotted logarithmically we obtain approximately a straight line, providing that we consider only concentrations below those which produce agglutination. Besides, these straight lines are more distinct in proportion as particle concentration, that is, adsorptive surface diminishes. Finally, they have all the same slope.

The results are shown in Fig. 15.

For gamboge as well as for mastic, the monovalent Na and K ions lead to identical results; also the divalent ions Mg and Ba. The trivalent La and Al ions present some divergences which are due without doubt to hydrolysis of the aluminium salts. The remaining trivalent ions follow rather indifferent straight lines when plotted logarithmically.

The concentrations in this case are for the most part higher than the agglutination concentration. Nevertheless the first two measurements give for logarithmic coördinates an approximately straight line, parallel to those corresponding to the adsorption of the ions H, Ba, Mg, K, Na. Mathematically expressed we have:

$$\operatorname{Log}\left(1-\frac{U}{U_0}\right)=p\log C+K.$$

The straight lines obtained with gamboge are parallel to and lie between those obtained for mastic; the slope is in the neighborhood of ½.

$$\left(1-\frac{U}{U_0}\right)=AC^p.$$

The exponent p is independent of the nature of the cation and of the surface holding the cation. The coefficient A varies inversely with these two factors. For each substance the coefficient is the greater as the valence of the ion is higher, except for the H ion, whose activity lies between that of the tri- and di-valent ions. Moreover, it has been verified roughly that if we designate the values of the coefficient A for the mono-, di- and trivalent ions, respectively A_1, A_2, A_3, we find $A_2 = A_1^2$, $A_3 = A_1^3$.

Finally, the coefficients A corresponding to the gamboge are less than those found for mastic.

This is in agreement with the only difference occurring between these suspensions, *i.e.,* the lower stability of the mastic grains. The adsorption for the same concentration of ions is greater for mastic than for gamboge. The values of the constant A are given in the following table:

TABLE IV

Nature of Adsorbed Ion	Mastic $p = \frac{1}{2}$ A	Gamboge $p = \frac{1}{2}$ A
Na^+, K^+	3.6	3.2
Ba^{++}, Mg^{++}	12.6	10.4
La^{+++}	47.0(?)	31.6
H^+	14.4	12.6

From the mean of these results it is possible to determine the quantity of ions held by the particles as a function of the concentration. Let x be the quantity adsorbed by unit surface, c the concentration of the substance adsorbed from the liquid, and $\frac{d\alpha}{dc}$ the derivative of the surface energy with respect to c. Then from Gibbs' law we have:

$$x=-\frac{c}{RT}\frac{d\alpha}{dc}$$

which shows that if surface energy increases as the concentration increases, then concentration is less at the interface than in the solution; if the surface energy decreases with increasing concentration, there is, on the contrary, an accumulation of solute at the interface.

But we are able to calculate $\frac{d\alpha}{dc}$. When the concentration of ions of the intergranular liquids is varied, the ionic atmosphere which surrounds each granule is itself modified in the same way. This change, as we have seen, comes into evidence in studying the migration of particles in an electric field.

Calling V the difference of potential of the double layer which surrounds the particle, the mobility U is related to this difference of potential in the following way:

$$U = \frac{KHV}{4\pi\eta}$$

in which K represents a coefficient depending upon the specific inductive capacity, H the electric field and η the coefficient of viscosity.

The introduction of ions charge oppositely to the granule modifies its ionic atmosphere and probably diminishes the thickness of the double layer. The difference of potential V varies likewise in the same direction.

The surface tension is the result of both the cohesive and electric forces. As has already been seen, these two factors exert antagonistic effects. By calling dW_c the increase of potential energy of cohesion for a variation dS of the surface, the value relative to the forces of cohesion is:

$$\alpha_c = \frac{dW_c}{dS}.$$

By calling dW_e the variation of the potential electrical energy for a variation of surface dS, the value relative to the electric forces is:

$$\alpha_e = \tfrac{1}{2}CV^2 = \tfrac{1}{2}\sigma V$$

σ being the density of the charge.

The surface tension will then be:

$$\alpha = \frac{dW_c}{dS} - \frac{dW_e}{dS} = \alpha_c - \tfrac{1}{2}\sigma V$$

$$\frac{d\alpha}{dc} = \frac{1}{2}\sigma\frac{dV}{dc}$$

But we have seen that

$$\frac{dV}{dc} = \frac{dU}{dc},$$

U being the mobility of the particle. The experimental results relative to the variation of the mobility with the ionic concentration of the intergranular liquid indicate that the variation of V as a function of the concentration c is given by the relation:

$$V = kc^p$$

in which p is independent of the nature of the ion and of the surface, and is in the neighborhood of $\frac{1}{2}$.

Then

$$\frac{dV}{dc} = pkc^{p-1} \quad \text{from which} \quad \frac{d\alpha}{dc} = -Kc^{p-1}.$$

Substituting this value in the Gibbs' equation we have:

$$x = \frac{c}{RT}Kc^{p-1} = K'c^p.$$

There results thus the isotherm of Freundlich, in which the coefficient p is $\tfrac{1}{2}$.

3. *Actions of Radiations.*—In showing the action of light upon the equilibrium of adsorption of ions, it is natural to think of the determination of the mobility of particles in an electric field. It has been seen indeed that this mobility is determined by the relation:

$$U = \frac{KHV}{4\pi\eta}.$$

In order to make this study logical and systematic, it has been necessary to determine the variation with time, of the mobility of different suspensions subjected to different radiations. The time of the establishment of equilibrium ranges from 20 to 35 minutes. This time is too short to allow more than one determination of the mobility in a series of suspensions exposed to various radiations. Besides, measuring the mobility takes time, which may run into several minutes. When we follow the variation of mobility with time, there results quite a considerable uncertainty as to the range of the time corresponding to the mobilities observed. Hence, it is preferable to compare among themselves the mobilities of suspensions submitted to different radiations, these mobilities being determined at the end of a time greater than that for the establishment of adsorption equilibrium. This study has been carried out upon mastic and gamboge varying the nature of the cation and its concentration.

The ions studied were: H, La, Al, Ba, Mg, K and Na. In all these cases the radiations of the visible spectrum acted very differently. The blue and the red radiations act antagonistically. The results are analogous for both gamboge and mastic.

Represent by U_λ the mobility of the granules of suspensions exposed to radiations λ (red), by U_λ' that corresponding to the suspensions exposed to radiation λ′ (blue), by U_o the mobility of the check suspensions left in the dark. These values represent the mobility of the suspensions half an hour after the introduction of the electrolyte in question. It may be taken for granted that the adsorption equilibrium is established. The effect produced by the radiation in question may be measured by the value of the ratio U_λ / U_o.

It is found that this ratio is greater than unity for suspensions exposed to radiations of low frequency, and on the other hand smaller than unity for those which are submitted to radiations of high frequency.

With relation to the checks, the short wave lengths increase the quantity of ions fixed, while the long wave lengths diminish it.

The influence of the concentration of the ions upon the effect produced has been studied. In all cases investigated the influence is the same. The resulting value increases with concentration up to an optimum concentration, and drops at a concentration in the neighborhood of that which produces agglutination of the suspension.

The following figures have been found for different cations.

Gamboge

Normality	$\frac{U\lambda}{U_o}$	$\frac{U\lambda'}{U_o}$
H_2SO_4		
0.000046	1.08	0.90
0.00023	1.31	0.70
0.00092	1.05	0.75
0.0087	1.05	0.98 (agglutination)

GAMBOGE

Normality	$\frac{U\lambda}{U_o}$	$\frac{U\lambda'}{U_o}$	
H_2SO_4			
HCl			
0.0001	1.01	0.95	
0.0004	1.30	0.72	
0.002	1.10	0.86	
La^{+++}: $La(NO_3)_3$			
0.00001	1.03	0.96	
0.0001	1.10	0.89	
0.0003	1.30	0.72	
0.001	1.00	1.02	(agglutination)
Al^{+++}: $Al_2(SO_4)_3$			
0.00001	1.00	0.95	
0.0001	1.20	0.87	
0.002	1.30	0.74	
0.006	1.00	1.00	(agglutination)
Ba^{++}: $BaCl_2$			
0.0001	1.10	0.85	
0.001	1.10	0.75	
0.01	1.00	0.97	(agglutination)
Mg^{++}: $MgCl_2$			
0.0001	1.10	0.87	
0.001	1.20	0.69	
0.01	1.00	0.96	(agglutination)
K^+: KCl			
0.0001	1.00	1.00	
0.001	1.10	0.87	
0.01	1.20	0.65	
0.07	1.00	1.00	(agglutination)
Na^+: NaCl			
0.0001	1.00	1.00	
0.001	0.80	1.10	
0.01	0.69	1.15	
0.1	—	—	(agglutination)

MASTIC.—The values indicated by U_λ/U_o correspond approximately to λ the optimum effect.

TABLE V

Electrolyte	Concentration in Normality	$\frac{U_\lambda}{U_o \text{ (red)}}$	$\frac{U_\lambda}{U_o \text{ (blue)}}$
H_2SO_4	0.000228	1.40	0.70
HCl	0.000380	1.30	0.68
$La(NO_3)_3$	0.000250	1.32	0.70
$Al_2(SO_4)_3$	0.000153	1.20	0.80
$BaCl_2$	0.0040	1.30	0.80
NaCl	0.01	1.20	0.80
KCl	0.01	1.22	0.78

These results show that the effect produced by the radiation to which the suspension is exposed passes through an optimum for a concentration in the neighborhood of that which causes agglutination of the particles.

Whatever may be the valence of the adsorbed ions, the maximum intensity of the action is the same. The optimum effect oscillates between 25 and 30 per cent but the preceding results do not indicate any systematic variation with the valence of the adsorbed cation. The course of this variation and the existence of an optimum is easily explained if one remembers that the velocity of adsorption is higher the greater the concentration of the cation. Now the time which the different operations require (addition of electrolyte, filling the flasks and placing them in the thermostat) may be more or less important. When the concentration of the electrolyte is in the neighborhood of the critical agglutination concentration adsorption occurs very rapidly and when the suspensions are exposed to the action of radiation, equilibrium is already established. On the other hand, when the concentrations of the electrolyte are very weak, the effect produced is very small, and if the light produces any modification it is only extremely feeble. It is thus that its action may manifest itself by the existence of an optimum.

The curves of the adsorption of ions may be traced for suspensions submitted to the action of various rays. Utilizing logarithmic coördinates, we find in general that a straight line results, represented by the equation:

$$\text{Log}\left(1-\frac{U_\lambda}{U_o}\right)=Kp\log C$$

in which U_λ represents the mobility of the grains of the suspension submitted to radiation of wave length λ for a concentration of ions C, and U_o the mobility before the introduction of the electrolyte. Concentrations greater than those for which the optimum effect is obtained do not obey the linear relation.

We have then:

$$\left(1-\frac{U_\lambda}{U_o}\right)=AC^p.$$

The exponent p is the same for all the curves; it is independent of the ions considered, of the wave length of the light, and also of the nature of the suspension. It is always approximately equal to ½.

The values of the parameter A for mastic are greater than those obtained for gamboge. However, for each substance and for each ion considered, the value of the parameter A_o corresponding to suspensions not subjected to any radiation, has a value intermediate between that obtained for the suspensions exposed to red radiations on the one hand and blue on the other.

By reason of the limited number of determinations for each adsorption curve, the verification of the preceding formula is incomplete.

There seems, moreover, to be a relation between the effect produced by light and the action of electrolytes. Let U_λ be the mobility of the suspension with the electrolyte and submitted to radiations of wave length λ; U_o the mobility in the absence of electrolyte and in the dark; and U' the mobility of the suspension with the addition of electrolyte but left in the dark. Then we have for each wave length:

$$\frac{U_o-U}{U_o-U'}=\text{constant}$$

The effect due to the light for unit action of electrolyte is constant. This is quite in conformity with the above results, which show that:

$$\left(1-\frac{U_\lambda}{U_o}\right)=A_\lambda C^p \quad \text{and} \quad \left(1-\frac{U'}{U_o}\right)=A'C^p$$

by dividing one of these by the other, we have:

$$\frac{U_o-U_\lambda}{U_o-U'}=\frac{A_\lambda}{A'}=\text{constant}$$

for a determined electrolyte and frequency of radiation.

Influence of temperature.—The change produced by light diminishes as the temperature of the illuminated suspension is raised. In the neighborhood of + 6° the observed effect is, according to the particular case, 1.5 to 2 times more intense than at 28°. On the average, the experimental results indicate that at 6° the effect is about 35 per cent, while at 28° it is no more than 20 per cent. This result is without doubt the consequence of the fact that temperature accelerates the adsorption process. It has been rather roughly verified that the position of the optimum is displaced towards the weak concentrations when the temperature is raised.

Influence of the concentration of particles.—Outside of experimental error we find on studying the influence of the number of particles per cubic centimeter that the very concentrated suspensions are nearly insensitive to the action of different radiations. This result is quite logical: the superficial layers hit by the rays protect the interior parts against the action of light.

Instability of the change produced.—The change produced by radiation upon the adsorption equilibrium is not stable; that is, the suspension when removed from the action of the light to which it has been exposed slowly loses the change which has been produced, disappearance being almost complete in from 3 to 5 hours.

The mobility of the particles of suspensions submitted to the action of red radiation diminishes in the direction of the check suspension. On the contrary the mobility of grains of the suspensions submitted to blue radiation increase toward the same limit. Apart from experimental errors this variation is exponential.

Once the equilibrium is thus established, if we once more subject the flask to the action of radiations, no further change is produced.

Applications to Biology

If the results obtained in the preceding experiments are susceptible of generalization, it might be said that light shows upon suspensions and colloidal solutions antagonistic actions; short wave length radiations destroy their stability, radiations of long wave length, on the contrary, increase it.

If it were the same for all colloids it would be easy to explain phenomena relative to the action of radiations upon tissues or upon living cells. Protoplasm which beyond doubt has a micellular structure, owes its existence to the stability of its constituent micells. All agents acting to diminish this stability should affect profoundly the activity of the protoplasm. This action may go as far as the total destruction of its activity, if the change of the mechanism of the forces of cohesion reach the coagulation point.

The action of light upon the cellular protoplasm is particularly characteristic for high frequencies. Ultra-violet rays are, indeed, very active and may energetically coagulate it, which is in conformity with the generalization suggested.

It is important to note that the repeated action of radiation of short wave length is equivalent to that of an elevated temperature.

In the domain of vegetable biology the application of these considerations is even more extensive. As LeClerc du Sablon [12] has shown, the principal functions of plant life may very probably be attributed to osmotic processes.

The intensity of the exchanges between various cells should be a function of the degree of permeability of the protoplasm. Now, the action of light upon this factor is evidenced by many experiments. Lepeschkin,[13] for example, has shown that light favors exosmosis across the struma of bean leaves. The permeability of the protoplasm is, therefore, increased. The same thing is found when the leaves of *Elodea* are exposed to sunlight and immersed in a very dilute solution of eosin; they become very strongly colored red, while similar leaves placed at the same temperature in the dark remain completely uncolored. The protoplasm of the vegetable cell reacts when exposed to the light, becoming more permeable.

These facts agree perfectly with the results on the action of light upon suspensions, if one extrapolates them to the protoplasmic micells and takes into account the degree of dispersion of the latter; that is to say, the permeability of protoplasm may be increased by radiations of long wave length. In view of the repartition of energy in the spectrum it is not surprising, then, that sunlight produces the same effect.

Plant functions other than absorption present analogous phenomena. Transpiration, for example, is a function of the radiation to which the plant is submitted. Wiesner [14] has studied the influence of light upon the transpiration of plants with chlorophyll and without chlorophyll. He has shown that this substance does not play an essential rôle in the phenomena and that it was even possible to find plants without chlorophyll whose transpiration was more sensitive to light than that of the former. In all these cases light increases the quantity of water transpired by the plant. If the intensity of transpiration is attributed to the protoplasmic permeability it is no longer difficult to understand the manner in which light acts, since it is possible to explain how the light modifies this latter factor. It appears then that the extrapolation to protoplasmic micells, of the results obtained with suspensions, gives an explanation of certain facts relative to the action of light in biological phenomena.

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Effect of Emulsoids on Colored Solutions

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The color of the solution of a colored substance of small molecular weight is little or not at all affected by the presence of an emulsoid which does not react chemically with the colored substance and which does not change the hydrogen ion concentration of the solution. When the colored substance has a large molecular weight, the presence of an emulsoid may influence the color of the solution in a number of ways. Should the colored solution be a suspensoid, the emulsoid will protect it from coagulation, as for example, gelatin protects colloidal gold solution. Should an insoluble colored substance be liberated from its soluble form the emulsoid will prevent its precipitation, as is the case when an acid solution of Nile blue is made alkaline in the presence of egg albumin. Finally, if the colored substance happens to fade on standing, the emulsoid may retard the rate of fading. This is true of methyl violet and gum arabic in alkaline solution. In all such cases the emulsoid exerts its influence by retarding or preventing some change which would take place in its absence, and consequently the color of the solution containing the emulsoid will differ from that of the same solution containing no emulsoid.

In this paper, however, we will describe quite a different kind of influence of emulsoids, an influence which depends on an equilibrium between the emulsoid and the colored substance.

In connection with the colorimetric determination of hemoglobin as alkaline hematin, we attempted to use as the standard of comparison pure alkaline hematin solution prepared by dissolving crystalline hemin in alkali. To our surprise we found that the color of the pure hematin solution was much weaker than that of the solution prepared from the corresponding amount of hemoglobin. Since the only difference between the two solutions was that the one prepared from hemoglobin contained a protein, globin, while the other contained, of course, no protein, it was clear that the globin increased the color of alkaline hematin. Addition of serum, egg white, gelatin and other proteins to the pure hematin solution was found to have a similar, though quantitatively different, effect. This led us to try other emulsoids such as gum arabic, starch, agar agar, etc., and all these were found to influence the color intensity of the alkaline hematin solution. A few exploratory experiments with another colored substance, congo red, gave similar results.

The influence of emulsoids on the color of alkaline hematin and congo red * solutions cannot be ascribed to a change in the alkalinity, for such a change of alkalinity as might be caused by the addition of the emulsoid was shown to have no appreciable effect in itself on the color of the solution. Moreover, the color of alkaline hematin and congo red produced on the addi-

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* On the color changes of benzopurpurin in the presence of protective colloids, see J. Alexander, *J. Soc. Chem. Ind.*, 30, 517 (1911); also Seventh International Congress of Applied Chemistry. J. A.

tion of an emulsoid cannot be obtained in its absence by mere change of reaction. Hematin and congo red are acids and they should not combine with protein, which in alkaline solution also behaves as an acid. Chemical combination of hematin and congo red with the polysaccharides is even more unlikely. That emulsoids of entirely different nature, such as egg albumin and gum arabic are, should exert a similar influence on the same colored substances shows that the influence is physical and not chemical.

In the search for colored substances upon which emulsoids have a marked effect, we surveyed about 100 colored substances, mostly dyes and indicators, using gum arabic as the emulsoid. The majority of the colored substances we studied were little or not at all affected by the gum. Some showed increase, others showed decrease in intensity, while still others showed great change in shade without much change in intensity.

Although we have used only gum arabic in the routine survey on account of its low buffer value and the consequent small change in hydrogen ion concentration when it is added to the colored solution, the results obtained are generally true also for other emulsoids, proteins and polysaccharides. Soaps in amounts which do not produce turbidity, however, have practically no influence on colored solutions. The chief factors which determine whether or not a given colored substance will be influenced by a given emulsoid must be, of course, the size and configuration of the molecule of the colored substance as well as of the emulsoid. The reaction of the solution and the concentration of the emulsoid are, however, also important. The same emulsoid may cause a decrease at one concentration and an increase at another concentration. For example, the color of alizarin red in alkaline solution is decreased by the addition of a small amount of gum arabic but is increased by larger amounts of the same emulsoid.* Again, other things being equal, the emulsoid may have no effect at one reaction but exert a marked influence at another reaction. Thus, the color of congo red in alkaline solution is not increased until the p_H of the solution is about 12.

There are two ways in which a colored solution may be influenced physically by the emulsoid: (1) adsorption of the colored substance by the emulsoid, and (2) adsorption of the emulsoid by the colored substance. In the former case a layer of the colored substance is formed around the particles of the emulsoid, while in the latter case the reverse is true. For convenience, the former will be called adsorption of the first kind, while the latter will be called adsorption of the second kind. The color of the adsorption complex in either case may differ in intensity and in shade from that of the particle of the free colored substance.

Since the adsorption complex, the free colored substance and the emulsoid, all remain dispersed, it is not easy to determine by analytical methods the concentration of these components. However, if we make certain assumptions regarding the color value of the adsorption complex as compared with that of the free colored substance, we can deduce from colorimetric measurements certain relations which agree well with the theory of adsorption.

CASE 1. ADSORPTION OF THE COLORED SUBSTANCE BY THE EMULSOID

Let the concentration of the total colored substance $= C_t$,
" " " " " adsorbed colored substance $= C_a$,
and " " " " " emulsoid $= E$.

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* Deflocculation may accompany adsorption. J. A.

Then, applying the usual adsorption equation,

$$\frac{C_a}{E} = a(C_t - C_a)^{\frac{1}{n}} \tag{1}$$

$$C_a = aE(C_t - C_a)^{\frac{1}{n}} \tag{2}$$

If C_a is small and negligible compared with C_t then

$$C_a = aEC_t^{\frac{1}{n}} \tag{3}$$

If the color value of the free colored substance is negligible in comparison with that of the adsorbed colored substance, then the color value of the solution is shown in the following equation.

$$V = K_1C_a \tag{4}$$

Substituting (3) in (4) and replacing K_1, a and E by a single constant K, then

$$V = (K_1aE)C_t^{\frac{1}{n}} = KC_t^{\frac{1}{n}} \tag{5}$$

Since $\frac{1}{n}$ is less than 1, it is readily seen from Equation (5) that the *relative* color value V would decrease with increasing total concentration C_t of the colored substance, the concentration of the emulsoid E being constant. In other words, there will be no proportionality between the total concentration of the colored substance and the color value, unless the concentration of the emulsoid is so large that all the colored substance is adsorbed.

CASE 2. ADSORPTION OF THE EMULSOID BY THE COLORED SUBSTANCE

Let the concentration of the total emulsoid $= E$,
" " " " adsorbed emulsoid $= e$,
and " " " " colored substance $= C$.

Then, applying the usual adsorption equation,

$$\frac{e}{C} = a(E - e)^{\frac{1}{n}} \tag{6}$$

If e is small and negligible compared with E, then

$$\frac{e}{C} = aE^{\frac{1}{n}} \tag{7}$$

Let the color value of the solution containing no emulsoid = 1 and the color value of the solution containing emulsoid $= V$, then the increase due to adsorbed emulsoid $I = V - 1$. Assuming that the increase is proportional to the amount of emulsoid adsorbed per unit of colored substance, then

$$I = V - 1 = K_1\frac{e}{C} \tag{8}$$

Substituting (7) in (8) and replacing K_1 and a by a single constant, K,

$$I = (K_1a)E^{\frac{1}{n}} = KE^{\frac{1}{n}} \tag{9}$$

From Equation (9) it is clear that the increase in the relative color value (I) depends only on the concentration of the emulsoid and is independent, within limits at least, of the concentration of the colored substance. It follows from this that the proportionality between the color value of the solution and the concentration of the colored substance holds in the presence as well as in the absence of the emulsoid.

The quantitative relationship between the concentration of the emulsoid and the intensity of the colored solution for a number of substances has been studied. At least two series of measurements were made for each colored substance with a given emulsoid. In one series the concentration of the emulsoid was varied, the concentration of the colored substance remaining constant. In the other series the relation was reversed.

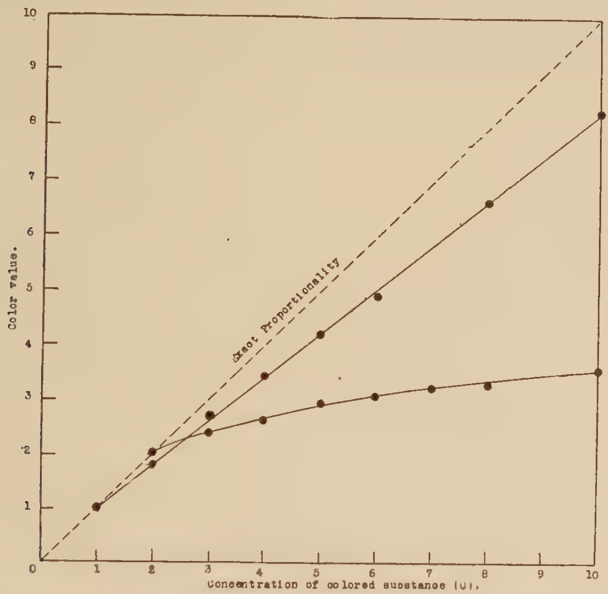

FIG. 1.—Relation between color value and concentration of colored substance in the presence of a submaximal amount of emulsoid.

Upper curve: Tumeric. C c.c. of 0.2% tumeric solution in alcohol + 2 c.c. 5% gum arabic + 5 c.c. 10% NaOH, made up to 50 c.c.

Lower curve: Iodine. C c.c. 0.001 N iodine in 0.02% KI + 3 c.c. 0.1% starch + 1 c.c. 10% KI + 1 c.c. N HAc + NaAc, made up to 50 c.c.

As an example of adsorption of the first kind the reaction between iodine and starch or other polysaccharides may be mentioned. The change of color of a dilute iodine solution from faint yellow to intense blue upon the addition of starch is so striking that iodo-starch was at one time regarded as a chemical compound. Since Küster showed that the amount of iodine taken up by starch varied with the concentration of the iodine solution in equilibrium with it, opinion has been divided as to whether iodo-starch is a solution or an adsorption compound.[1] The concept of solution as applied to iodo-starch is distinctly vague. Since the iodo-starch reaction takes place only in the presence of water, for starch does not become blue when suspended in an alcoholic solution of iodine, it is evident that the reaction is one of starch as an emulsoid, a colloidal solution of starch in water, and not of starch as a solid. According to the current concept of emulsoids, a starch solution should consist of starch particles, containing water, suspended in a very dilute solution of starch in water. Should the iodine molecules enter the starch particles, the process may be considered as one of solution. But as the iodine molecules are thus surrounded by starch molecules, the complex may also be considered as an adsorption compound, in which iodine is the adsorbent (adsorption of the second kind). Should the iodine molecules be held on the surface of the starch particles, the complex is in no sense a solution, but is an adsorption compound in which starch is the adsorbent (adsorption of the first kind).

We are aware that the iodide ion plays an important part in the iodo-starch reaction, for the reaction is far more sensitive in the presence of potassium iodide. The color of the iodo-starch depends also on the state of aggregation of the starch particles, for two starch solutions of the same strength but of different origin will give different amounts and shades of color. It is possible that the iodo-starch reaction is more complicated than either simple adsorption or solution, and conclusive proof awaits more rigorous methods of analytical chemistry than the colorimetric method described in this paper. But when all the variable factors are kept constant, the results of colorimetric measurements are uniform and reproducible, and point unmistakably to the conclusion that iodo-starch is an adsorption compound of iodine on starch.

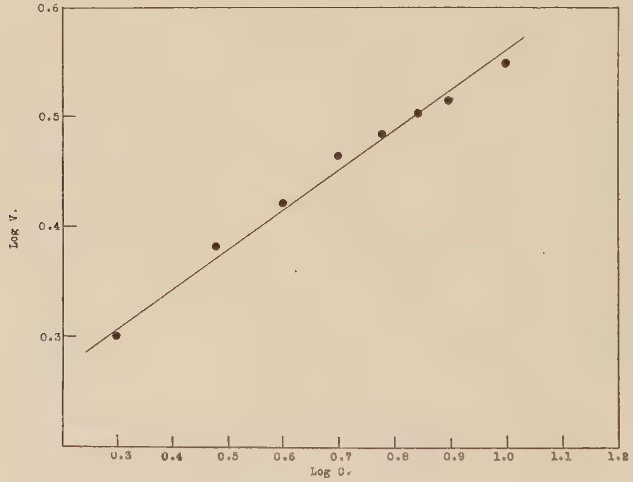

Fig. 2.—Adsorption of iodine by starch.

In Table I and Fig. 1 it will be noted that the color value of the iodo-starch solution is far from being proportional to the total concentration of iodine when the concentration of starch is constant. The color value-concentration curve is in fact an adsorption curve and the log V-log C curve (Fig. 2) is a tolerably straight line when the concentration of starch is small and C_a is negligible in comparison with C_t. These facts are in harmony with the equations derived for the adsorption of the first kind.

TABLE I

Effect of Same Amount of Starch on Color of Different Amounts of Iodine

3 c.c. 0.1 per cent starch + C c.c. 0.001 N I_2 + 1 c.c. N (HAc + NaAc) + 1 c.c. 10 per cent KI, made up to 5.0 c.c.

C	V	Log C	Log V
2*	2.000	0.301	0.301
3	2.417	0.477	0.383
4	2.633	0.602	0.421
5	2.923	0.699	0.466
6	3.054	0.778	0.485
7	3.183	0.845	0.503
8	3.269	0.903	0.514
10	3.840	1.000	0.549

* The color value of this solution is arbitrarily taken as 2.

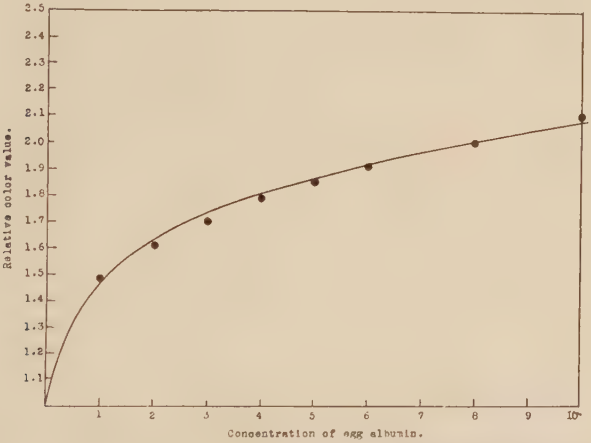

Fig. 3.—Color value of congo red solutions containing different amounts of egg albumin.

TABLE II

Effect of Egg White on Color of Congo Red

5 c.c. 0.025 per cent congo red + E c.c. 5 per cent egg white + 4 c.c. 10 per cent NaOH made up to 50 c.c.

E	V	I	Log E	Log I
0*	1.000	0		
1	1.484	0.484	0	$\bar{1}.685$
2	1.602	0.602	0.301	$\bar{1}.780$
3	1.698	0.698	0.477	$\bar{1}.844$
4	1.788	0.788	0.602	$\bar{1}.897$
5	1.850	0.850	0.699	$\bar{1}.930$
6	1.911	0.911	0.778	$\bar{1}.960$
8	2.010	1.010	0.903	0.004
10	2.100	1.100	1.000	0.041

* The color value of this solution is arbitrarily taken as 1.

The effect of emulsoids on most of the colored substances which we have studied can be explained as adsorption of the emulsoid by the colored substances. With some of these, congo red, hematin, erythrosin, trypan red, etc., the results of colorimetric measurements fit Equation (9) closely. With some others, alizarin red and turmeric for example, this equation fails to apply, but that we are dealing with adsorption of the second kind may still be inferred from other facts.

The result of the experiment on congo red and egg albumin is shown in Table II and Fig. 3. It will be noted that the *I-E* curve (Fig. 3) is a typical adsorption curve and that the log *I*-log *E* curve (Fig. 4) is a straight line. The relation between *I* and *E* can be expressed by the equation:

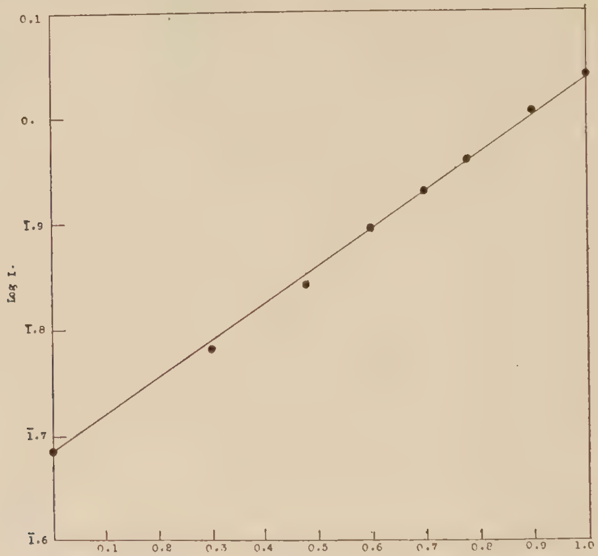

Fig. 4.—Adsorption of egg albumin by congo red.

$$I = V - 1 = 0.464E^{0.374}$$

which holds for concentrations of congo red from 1 to 5 c.c. of 0.1 per cent solution and concentrations of egg albumin from 1-10 c.c. of 5 per cent solution in 50 c.c. With concentrations outside of these limits the equation no longer holds. It will be remembered that in the derivation of Equation (9) two assumptions were made: (1) that the increase in color value is proportional to the amount of adsorbed emulsoid and (2) that the amount of adsorbed emulsoid is negligible compared with the total emulsoid in solution. These assumptions can hold, of course, only within certain limits. Similar result was obtained with congo red using 0.5 per cent gum arabic instead of 5 per cent egg albumin (Table III and Fig. 5).

The results of our experiments on hematin, alizarin red and turmeric, using either egg albumin or gum arabic as the emulsoid are shown in Tables IV-VIII. The log *E*-log *I* curves for hematin (Fig. 5) are tolerably straight lines. That for turmeric (Fig. 6) is unquestionably a curve. But it covers a

TABLE III

Effect of Gum Arabic on Color of Congo Red

1 c.c. 0.1 per cent congo red + E c.c. 0.5 per cent gum arabic + 5 c.c. 10. per cent NaOH made up to 50 c.c.

E	V	I	Log E	Log I
0*	1.000	0		
1	1.104	0.104	0	$\bar{1}.017$
2	1.173	0.173	0.301	$\bar{1}.238$
3	1.250	0.250	0.477	$\bar{1}.398$
4	1.311	0.311	0.602	$\bar{1}.493$
6	1.382	0.382	0.778	$\bar{1}.582$

* The color value of this solution is arbitrarily taken as 1.

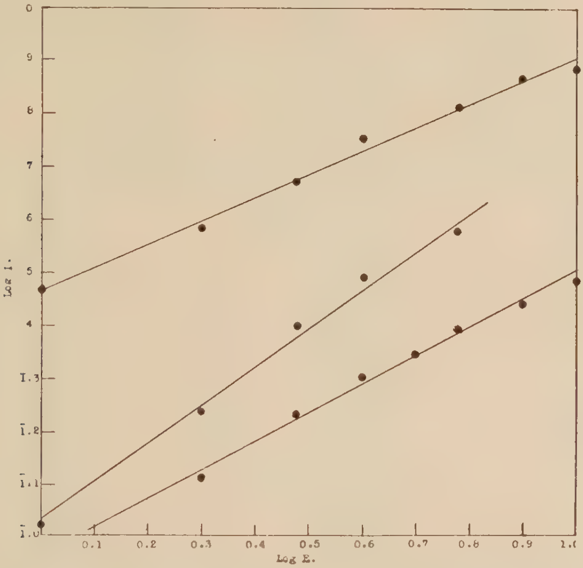

Fig. 5.—Adsorption of emulsoids by colored substances.
Upper curve: hematin + egg albumin.
Middle curve: congo red + gum arabic.
Lower curve: hematin + gum arabic.

TABLE IV

Effect of Egg White on Color of Alkaline Hematin

2 c.c. 0.1 per cent hemin + E c.c. 5 per cent egg white + 5 c.c. 10 per cent NaOH made up to 50 c.c.

E	V	I	Log E	Log I
0*	1.000	0		
1	1.293	0.293	0	$\bar{1}.467$
2	1.383	0.383	0.301	$\bar{1}.583$
3	1.471	0.471	0.477	$\bar{1}.673$
4	1.563	0.563	0.602	$\bar{1}.751$
6	1.655	0.655	0.778	$\bar{1}.816$
8	1.734	0.734	0.903	$\bar{1}.866$
10	1.760	0.760	1.000	$\bar{1}.881$

* The color value of this solution is arbitrarily taken as 1.

TABLE V

Effect of Gum Arabic on Color of Alkaline Hematin

2 c.c. 0.1 per cent hemin + E c.c. 5 per cent gum arabic + 5 c.c. 10 per cent NaOH made up to 50 c.c.

E	V	I	Log E	Log I
0*	1.000	0		
1	1.083	0.083	0	$\bar{2}.919$
2	1.133	0.133	0.301	$\bar{1}.124$
3	1.171	0.171	0.477	$\bar{1}.233$
4	1.200	0.200	0.602	$\bar{1}.301$
5	1.221	0.221	0.699	$\bar{1}.344$
6	1.245	0.245	0.778	$\bar{1}.389$
8	1.275	0.275	0.903	$\bar{1}.439$
10	1.304	0.304	1.000	$\bar{1}.483$

* The color value of this solution is arbitrarily taken as 1.

TABLE VI

Effect of Egg White on Color of Alizarin Red

1 c.c. 0.1 per cent alizarin red + E c.c. 5 per cent egg white + 5 c.c. 10 per cent NaOH, made up to 50 c.c.

E	V	I
0*	1.000	0
0.5	0.939	—0.061
1	0.916	—0.084
2	0.859	—0.141
3	0.834	—0.166
4	0.812	—0.188
5	0.787	—0.213
6	0.785	—0.215
7	0.799	—0.201
8	0.810	—0.190
10	0.827	—0.173
15	0.853	—0.147
20	0.880	—0.120
30	0.935	—0.065
40	0.961	—0.039

* The color value of this solution is arbitrarily taken as 1.

TABLE VII

Effect of Gum Arabic on Color of Alizarin Red

1 c.c. 0.1 per cent alizarin red + E c.c. 5 per cent gum arabic + 5 c.c. 10 per cent NaOH, made up to 50 c.c.

E	V	I
0*	1.000	0
0.5	0.789	—0.211
1	0.716	—0.284
1.5	0.689	—0.311
2	0.706	—0.294
3	0.744	—0.256
4	0.822	—0.178
5	0.880	—0.120
6	0.944	—0.056
8	0.986	—0.014
10	1.016	+0.016
15	1.043	+0.043
20	1.068	+0.068

* The color value of this solution is arbitrarily taken as 1.

TABLE VIII

Effect of Gum Arabic on Color of Turmeric

1 c.c. 0.2 per cent turmeric + E c.c. 5 per cent gum arabic + 5 c.c. 10 per cent NaOH made up to 50 c.c.

E	V	I	Log E	Log I
0*	1.000	0		
1	1.113	0.113	0	$\bar{1}.053$
2	1.266	0.266	0.301	$\bar{1}.425$
4	1.506	0.506	0.602	$\bar{1}.704$
6	1.680	0.680	0.778	$\bar{1}.833$
8	1.830	0.830	0.903	$\bar{1}.919$
10	1.961	0.961	1.000	$\bar{1}.983$
15	2.217	1.217	1.176	0.085
20	2.370	1.370	1.301	0.137
30	2.499	1.499	1.477	0.176
40	2.608	1.608	1.602	0.206

* The color value of this solution is arbitrarily taken as 1.

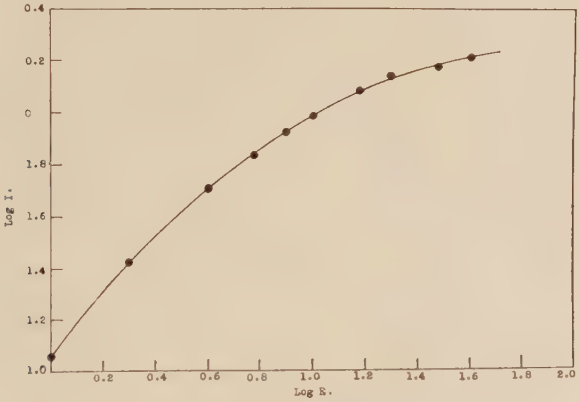

Fig. 6.—Adsorption of gum arabic by turmeric.

wide range of concentrations of the emulsoid, and the slight deviation from lineality may be explained by the failure of the assumptions made in the derivation of Equation (9). No attempt was made to interpret the *E-V* curves (Fig. 7) for alizarin red which show a minimum, for evidently no simple relation between color intensity and adsorption of the emulsoid could be assumed in such a case. The color value of solutions of both tumeric and alizarin red is, however, approximately proportional to the concentration of the colored substance in the presence as well as in the absence of the emulsoid (Fig. 1), and we must conclude either that the emulsoid is adsorbed on the colored substance or that the colored substance is *completely* adsorbed by the emulsoid. The latter explanation is, however, improbable, since the same *V-C* curve is obtained with very small amounts of the emulsoid.

Sometimes, the presence of an emulsoid decreases the color intensity of the solution of the colored substance. The influence of gum arabic on China blue is an example. The results of colorimetric measurement in this case also fit the equation for the adsorption of the second kind (Table IX and Figs. 8-9).

TABLE IX

Effect of Gum Arabic on Color of China Blue

1 c.c. 0.1 per cent China blue + E c.c. 5 per cent gum arabic + 1 c.c. 10 per cent HCl made up to 50 c.c.

E	V	I	Log E	Log (—I)
0.0 *	1.000	0		
0.5 *	0.962	—0.038	1.699	$\bar{2}.580$
1	0.928	—0.072	0	$\bar{2}.857$
2	0.887	—0.113	0.301	$\bar{1}.053$
3	0.832	—0.168	0.477	$\bar{1}.225$
4	0.800	—0.200	0.602	$\bar{1}.301$
6	0.768	—0.232	0.778	$\bar{1}.366$
8	0.760	—0.240	0.903	$\bar{1}.380$

* The color value of this solution is arbitrarily taken as 1.

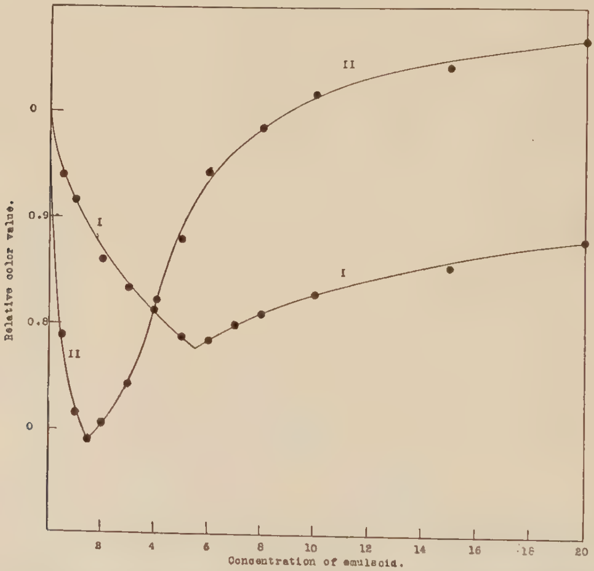

Fig. 7.—Color value of alizarin red solutions containing different amounts of (I) Egg albumin and (II) Gum arabic.

TABLE X

Relative Effect of Emulsoid on Color Value of Congo Red

1 c.c. 0.1 per cent congo red + 100 mgs. emulsoid + 5 c.c. 10 per cent NaOH, made up of 50 c.c.

Emulsoid	Color Value
None	1.000
Starch	1.062
Dextrin	1.063
Gelatin	1.317
Egg albumin	1.602
Agar-agar	1.700

The influence of different emulsoids on the same colored substance varies considerably (Table X). One is reminded of the influence which emulsoids exert on colloidal gold solution. Although the action of emulsoids on gold solution and that on congo red solution are different, the underlying cause is probably the same, namely, the formation of an envelope around the particle of the colored substance. Since the effect of emulsoids on colored substances such as congo red lends itself more readily to quantitative measurement than the protective action of emulsoids on gold solution, it would seem that the adsorption of the second kind described in this paper might furnish a basis for a new reaction which would serve the same purpose as does the gold reaction in clinical diagnosis.

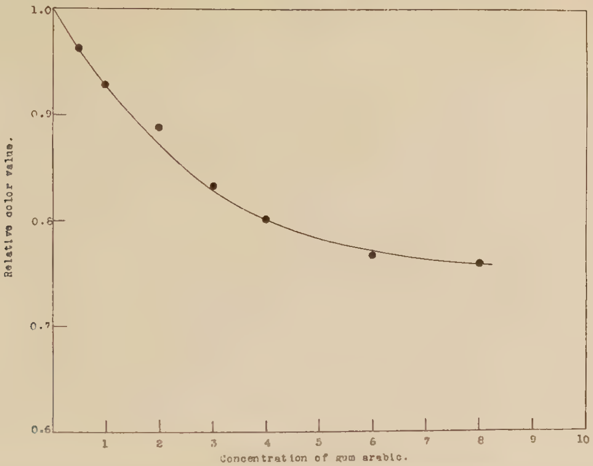

FIG. 8.—Color value of China blue solutions containing different amount of gum arabic.

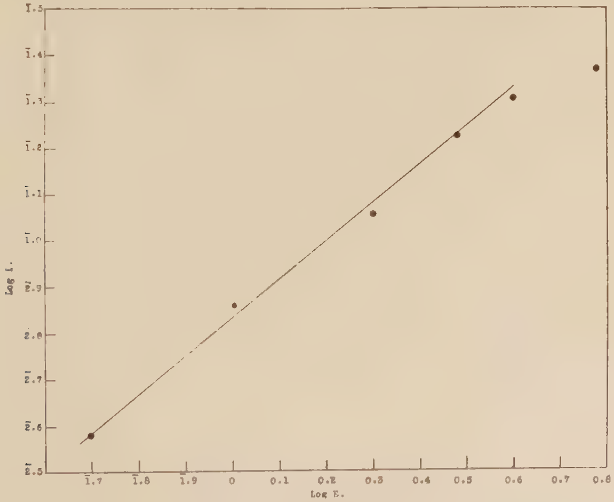

FIG. 9.—Adsorption of gum arabic by China blue.

The effect of different proteins and their derivatives on the same colored substance seems to depend on the size of the molecules. While the natural proteins have a marked effect on congo red, proteoses and peptones have only a slight effect and peptides have none. It would seem also that the adsorption of the second kind may serve as a test of the relative complexity of proteins and other emulsoids.

The so-called "protein error" has long been recognized in the colorimetric determination of hydrogen ion concentration. From the work reported in this paper, it is clear that the presence of emulsoids is a factor to be considered in colorimetry in general. If emulsoids have no influence on the colored substance in question, then the presence of an emulsoid would of course cause no error. If the emulsoid has an influence on the colored substance, then it will be necessary to ascertain whether the emulsoid is adsorbed on the colored substance or vice versa. In the former case, the color value will be proportional to the concentration of the colored substance provided the same amount of the emulsoid is present in the standard and in the unknown solution. In the latter case the color value will not be proportional to the concentration of the colored substance even when the same amount of the emulsoid is present in the standard and in the unknown solution.

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1. Küster, *Annal. d. Chemie v. Pharmacie,* 283, 360, and von Euler, *Kolloid Z.,* **31**, 81, are inclined to regard iodo-starch as a solution, while Harrison, *Kolloid. Z.,* **10**, 15, Berczeller, *Biochem. Z.,* **84**, 106, and Lottermoser, *Z. angew. Chem.,* **34**, 427, are in favor of the adsorption theory.

Aerosols

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Aerosols are disperse systems in which the dispersion medium is a gas. The disperse phase may be solid—as in a smoky flame or a metallurgical fume—or it may be liquid, as in an atmospheric mist or cloud. It is convenient to denote as *clouds* or *cloudy aerosols* those systems in which the particles are too large to exhibit Brownian motion at the ordinary temperature and pressure, and to denote the more highly disperse systems as *smokes* or *smoky aerosols.*

Under certain conditions, an aerosol may become flocculated, the particles uniting to form loose aggregates or flocks that possess a network structure analogous to that of the gel that is formed by the coagulation of a hydrosol. Such flocks may be conveniently regarded as *aerogels.* Familiar instances are the flakes that are formed when metallic magnesium burns rapidly in air, and the accumulation of soot that forms in the flue of the domestic fireplace.

Disperse systems in gases possess both theoretical significance and industrial importance. In presenting this account of the nature and significance of aerosols, it will be convenient for us to study the manner of their formation, their structure and stability, and their general properties, particularly in relation to the properties and behavior of disperse systems in liquid and solid dispersion media. We will also consider the application of this information to the problems of the condensation and filtration of industrial fumes, and dust explosions. Other important applications—to meteorology and the use of smoke in warfare—receive full treatment elsewhere.

THE FORMATION OF AEROSOLS

An aerosol, like any other disperse system, can be formed either by the mechanical disintegration of a solid or liquid that is originally in a relatively coarse condition, or by the condensation of a molecularly disperse system—in this case, a gas or vapor.

Dispersion Processes.

When grain or sugar is ground in a mill—when, in dry weather, the air above a busy road is made dusty by traffic—when a volcano ejects fine dust and smoke into the air—when a wave of the sea, dashing against the foot of a cliff, bursts into spray—when the contents of a high-explosive shell detonate into dust—aerosols are being produced by the mechanical dispersion of solids or liquids.

Industrially, aerosols are most frequently produced by the disintegration of solids in attrition mills or disintegrators, and by the spraying (atomizing) of liquids. The dry grinding of a solid may be performed in many ways in which some of the particles are either torn apart by tension, while in others they are driven apart by crushing or shearing forces. Generally speaking, the efficiency with which the solid is disintegrated, and the degree of dispersion that is attained, are higher, the more rapidly the disintegrating force is applied.

Many sprays have been designed for reducing liquids such as water, oil, liquid metals, to a fine mist. These all depend for their action upon a sudden and violent collision between a jet of the liquid and either a solid surface (generally moving relatively at a high speed—*e.g.*, a rapidly rotating disc), a second jet of the liquid itself, or a jet of compressed gas. In a similar way, a bubble film breaks up into fine droplets when the bubble bursts, as in the formation of a mist during effervescence.

The degree of dispersion that can be produced with a given expenditure of energy can be increased by reducing the viscosity of the liquid—*e.g.*, by raising its temperature, or by diluting it with a liquid of comparatively low viscosity, or by lowering the surface tension (for instance, by the addition of a substance like saponin to an aqueous salt solution). If these alterations are impracticable, it will be necessary to increase the velocity of impact between the liquid and the disintegrating surface.

A great deal of work has to be done in order to reduce a solid or liquid to fine dust—first of all, in overcoming the forces of cohesion that originally hold the particles together, and then in distributing the particles throughout the dispersion medium. Mechanically produced aerosols, therefore, generally possess a relatively low degree of dispersion. They are also less uniform in structure than aerosols that are produced by the condensation of a vapor.

Condensation Processes.

Matter will remain gaseous as long as its molecules possess sufficient kinetic energy to overcome the forces of attraction or cohesion that tend to draw them all together into a compact liquid or solid mass. A gas will tend to condense if, and when, and where the kinetic energy of its molecules becomes too small—*i.e.*, if the temperature of the gas at any point falls below a certain value.

Surface cooling.—A gas may be cooled locally by contact with a cold surface, whether of another mass of gas, or of a liquid or solid. Such surface cooling depends upon the rate at which the entire volume of gas comes into contact with the cooling surface, and is generally a comparatively slow process. The rate of cooling depends, also, upon the heat capacity of the cold surface—*i.e.*, its specific heat and thermal conductivity. Clearly, when a mass of gas comes into contact with continuous liquid or solid surfaces that are relatively cold, condensation will produce a film of liquid or solid condensate. In the early stages of condensation, this film may be discontinuous and extremely finely divided, as in the case when metallic vapors condense rapidly upon the chilled wall of a glass container. It cannot, however, be regarded as an aerosol. An aerosol can be formed by surface cooling only when the cooling surface is itself a gas. To some extent, clouds are formed in nature by the slow mingling of a mass of warm, moist air with another mass of cold air.

Necessarily, the degree of dispersion of any condensate that is produced by surface cooling will be irregular, the particles that form first being larger than those that form later.

Surface cooling may occur almost simultaneously throughout a volume of gas, and thus simulate volume cooling. When the sun goes down after a warm day and the warm, moist, dusty air is robbed of the radiation that warmed it, it cools by radiation towards the sky. Radiation being most intense from the suspended dust particles, the cooling is confined almost entirely at first to the surface of these particles. It then extends, by conduction, to the surrounding gas molecules, and, when the dewpoint is reached in the immediate neighborhood of the dust particles, water vapor condenses upon them and a mist results. The degree of dispersion of such a mist will depend at first upon the size of the dust particles, and since, in still air, these may be considered to be uniform, it, also, will be fairly uniform.

Volume cooling.—The most satisfactory method of producing an aerosol by condensation is to cool the gas simultaneously throughout its entire volume. When a container filled with gas is enlarged suddenly—*e.g.*, during the expansion stroke of an internal combustion engine—the gas, by reason of the kinetic energy of its molecules, immediately expands until it occupies the enlarged space. The molecules, in separating further apart, perform work at the expense of their own kinetic energy, and, if the expansion is carried out so quickly that no heat enters from without during the process, the kinetic energy of the individual molecules, and, therefore, the temperature of the gas, will be diminished by an amount that will be proportional to the degree of expansion that the gas has undergone. Owing to the elasticity of the gas, this cooling effect will occur almost simultaneously throughout the entire volume of the gas. If, therefore, the degree of expansion is sufficient to reduce the temperature of the gas to below the dewpoint, the gas will tend to condense simultaneously at all points. For condensation to occur, it is necessary—as J. Aitken, C. T. R. Wilson and C. Barus * have shown [1]—for suitable condensation nuclei to be present, suspended in the gas. In the absence of nuclei, condensation occurs relatively slowly upon the walls of the containing vessel.

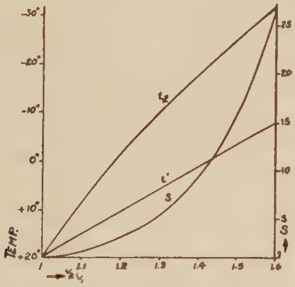

FIG. 1.—Variation of maximal cooling temperature t_2, equilibrium temperature t^1, supersaturation S, with ratio of volumes V_2/V_1 in the case of condensation of water vapor by adiabatic expansion.

Suitable condensation nuclei may be particles of dust, or smoke, or of various salts; they may be gaseous ions or, at high degrees of supersaturation, actual aggregates of the gas molecules themselves. They may be present before the gas is expanded, they may be added during the expansion, or they may be added subsequently.

After the expansion is completed, and if suitable nuclei be present, vapor rapidly condenses upon the nuclei. The degree of dispersion of the resulting aerosol depends upon the degree of supersaturation that is produced by the expansion, and upon the number and character of the nuclei that are present.

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* See paper by C. Barus, this volume. J. A.

Commencing with air saturated at a temperature $T_1 = 20°$ C., the degree of cooling $(T_1 - T_2)$ and the degree of supersaturation (S) produced by given expansion ratios $\frac{V_2}{V_1}$ are shown in Fig. 1.

$S = \frac{C_1}{C_2}$, where C_2 is the concentration of water vapor in the air at the final temperature T_2, and C_1 is the concentration of water vapor in the air immediately before expansion.

The actual amount of water vapor that is condensed by a given expansion of a volume of saturated air is determined by the degree of supersaturation that is produced. The number of droplets that will be formed from this vapor, and, therefore, their average size, will depend upon the number of suitable nuclei that are present in the vapor. Clearly, the droplets will be smallest when a small amount of vapor condenses upon a large number of nuclei.

In ordinary saturated air, at low expansions, cloudy condensation results, since dust particles are numerous. If the air be entirely freed from dust particles—for example, by filtration through a plug of cotton wool—no condensation will occur until the volume has been increased 25 per cent—*i.e.*, until the degree of supersaturation has become nearly 4.2 times as great (Fig. 1).

For expansions ranging from 1.25 to 1.34 $(S = 6.8)$, the vapor condenses in the form of fine rain. The size of the droplets varies throughout the process of condensation from about 200 μ radius, when $\frac{V_2}{V_1} = 1.25$, to 20 μ, when $\frac{V_2}{V_1} = 1.34$.

The nuclei upon which this rainy condensation occurs are gaseous ions. For expansions of from 1.25 to 1.28, water vapor condenses only upon negative ions. For expansions of from 1.28 to 1.34, it condenses upon positive ions.

The number of ions naturally present in ordinary air is very small. Consequently, the degree of dispersion is correspondingly low. If other gases are used, in which the natural degree of ionization is markedly different from that of air, very different degrees of dispersion may be obtained. With hydrogen, a very slightly ionized gas, no rainy condensation occurs between $\frac{V_2}{V_1} = 1.28$ and 1.4. With chlorine, which normally is more ionized than other gases, condensation between $\frac{V_2}{V_1} = 1.28$ and 1.4 is more cloudy.

In dust-free air, if the ionization be increased—*e.g.*, by X-rays or by radiation from radioactive substances—the degree of dispersion will be greatly increased, cloudy condensation being produced instead of fine rain. This fact has been employed very ingeniously by C. T. R. Wilson to make visible the paths of α and β particles travelling through supersaturated, and otherwise unnucleated, air. The particle ionizes the air as it passes through it, leaving behind it a trail of cloudy condensation.

When the degree of expansion of saturated air exceeds 1.4, cloudy condensation again sets in, and occurs until $\frac{V_2}{V_1} = 1.43$, after which the condensate becomes coarse again, the degree of dispersion diminishing rapidly as $\frac{V_2}{V_1}$ increases. When $\frac{V_2}{V_1} = 1.46$, the radius of the drop is about 0.6 μ.

The nuclei that operate at these degrees of expansion are electrically neutral, and are probably complex water molecules. Such nuclei appear to be formed in water vapor more readily when hydrogen is used instead of air.

Vapors other than water vapor behave similarly, the relation between the degree of expansion and the resulting degree of dispersion being characteristic and different for each substance.

Action of Condensation Nuclei.

It is reasonable to assume that these well-defined variations in the character of the condensation process are due in some way to the specific action of different kinds of condensation nuclei. In a homogeneous system, it is very difficult to induce a change of state—for example, crystallization from saturated solutions, or the condensation of unnucleated vapor. Some point of singularity, some nucleus or "free surface," is necessary to act as a center, from which the change can spread.

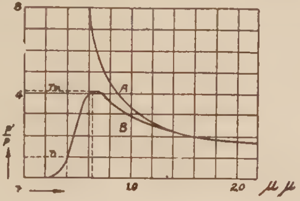

FIG. 2.—Vapor pressures of very small water droplets.

Little is known about the actual shape of nuclei, but it is reasonable to assume that liquid nuclei are spherical and, therefore, have a convex surface, while solid, crystalline nuclei may present a series of plane surfaces to the vapor, or, if irregularly crystalline or amorphous in structure, may at some point be concave. Vapor will condense more readily upon an irregular particle—*e.g.*, a dust particle—than upon one more regular or continuous.

The vapor pressures (p) above a plane surface, and (p') above a curved surface, whose radius of curvature is (r), are related to each other and to (r) by the expression[2]

$$\text{Log}\,.\,\frac{p'}{p} = \frac{2\sigma}{r\rho RT} \qquad (1)$$

where σ is the surface tension of the liquid,
ρ is the density of the liquid,
R is the gas constant,
and T is the absolute temperature.

The values of $\frac{p'}{p}$ for different values of r are plotted in curve A, Fig. 2, assuming that the surface is convex, and that p', therefore, is greater than p.

For a concave surface, p' would be less than p, so that $\frac{p'}{p}$ would possess values less than 1, and the curve would be inverted.

At a plane water surface at 0° C., the vapor pressure p is 6,000 dynes per square centimeter. For a water droplet of radius μ, the vapor pressure at 0° C., p' is 6,007.3 dynes per square centimeter—a negligible difference. We see from the curve, however, that, when the value of r has become 1.6 $\mu\mu$, $\frac{p'}{p} = 2$ — that is, p' is twice as great as p. As the radius is further diminished, p' increases with increasing rapidity.

Clearly, therefore, such small droplets would evaporate extremely rapidly at ordinary degrees of supersaturation. Conversely, it is impossible for vapor to condense upon them, unless the degree of supersaturation—that is to say, the density of the vapor—is very high. In the absence of nuclei, therefore, it is impossible for droplets to form—that is, for condensation to occur—unless, perhaps, at supersaturations of 8 or more, molecular aggregates exist of radius not less than 0.6 $\mu\mu$.

(At such extreme values of the curvature of the surface, it is probable that the surface tension has a different value from that of a plane surface. If we assume that σ is diminished for a convex surface of such small radius of curvature, then log. $\frac{p'}{p}$ is diminished, and consequently the value of $\frac{p'}{p}$ is smaller—that is, the increased vapor pressure of the droplet may not increase quite so rapidly at extremely small values of r.)

To induce condensation, therefore, it is necessary to introduce suitable nuclei that will reduce the pressure of the vapor at their surfaces. Such nuclei may be—

(a) Inert particles possessing plane surfaces, the vapor pressure at such a surface being equal to p, and, therefore, lower than the pressure of supersaturated vapor.

(b) Inert particles possessing porous surfaces, such that the radius of curvature of the pores is less than 1 μ—the value of r, at which, for a concave surface, the pressure of the vapor begins to be less than at a plane surface. Clearly, once a film of vapor molecules has formed by adsorption, vapor will condense upon such a surface, even although it be unsaturated, and, as the radius of curvature of the pores is further diminished, it will condense readily upon the pore surfaces, even from vapor at pressures far below its saturation point.

(c) Inert particles carrying an electrical charge—*e.g.*, ionized gas molecules. The presence of an electrical charge on the surface of a liquid opposes the surface tension, and, therefore, diminishes the vapor pressure, to an extent that is proportional to the fourth power of the drop.

For charged liquid surfaces,

$$\log. \frac{p'}{p} = \frac{1}{RT\rho}\left(\frac{2\sigma}{r} - \frac{c^2}{8\pi r^4}\right) \tag{2}$$

where c is the quantity of charge per square centimeter of surface.

The relation between $\frac{p'}{p}$ and r for charged droplets is shown in Fig. 2, curve B.

For a droplet of radius *r*, carrying unit charge, $\frac{p'}{p} = 1$, so that the vapor pressure of the charged drop is just equal to that of a plane liquid surface. If more vapor were to condense upon it, *r* would increase, and its vapor pressure would rapidly increase until, at a radius of 0.63 μμ, the vapor pressure would reach a maximum, *p′* being about four times as great as *p*. Condensation is, therefore, impossible upon such charged droplets, if the radius is less than 0.63 μμ.

Condensation is only possible if the vapor pressure diminishes as *r* increases—that is, when *r* is greater than 0.63 μμ.

The pressure at which condensation to form a charged droplet first becomes possible, therefore, is that corresponding to radius r_m. This is 4.2 times that above a plane surface, a value which corresponds well with that obtained experimentally.

It is difficult to understand why, at a supersaturation of 4.2, water vapor condenses exclusively upon the negative ions, and, at a supersaturation of 6, upon positive ions. It would be more reasonable to expect that condensation would occur more readily upon positive ions, since these are generally the larger, and condensation occurs more freely the larger the particle. Other vapors generally condense more readily upon positive ions. Apparently, the anomalous behavior of water vapor is due to some specific relationship between the character of the molecules of the vapor or of the "indifferent" gas and the size of the electrical charge. In this connection, it is interesting to note that, when ultra-violet light passes through air, it ionizes the constituent gases, and at the same time produces traces of such hygroscopic compounds as NH^3, H_2O_2, NO_2, etc. These form good nuclei for the condensation of water vapor.

(d) Substances that have a strong chemical affinity for the vapor. With water vapor, for example, hygroscopic substances, such as NaCl, SO_3, combine with molecules of the vapor to form droplets possessing a lower vapor pressure, upon which more vapor easily condenses, even at low degrees of supersaturation—in fact, from unsaturated vapor. Droplets so formed have a permanently lowered vapor pressure, although it increases slightly as the drop becomes diluted by further condensation. Such droplets, therefore, remain stable even when the air has become unsaturated. Atmospheric water vapor condenses to form a mist or cloud, because of the presence of hygroscopic nuclei—*e.g.*, NaCl, SO_3—in the atmosphere. The stability of a city fog, often in a highly unsaturated atmosphere, has been attributed to the lowered vapor pressure of the droplets, owing to the presence of H_2SO_4 dissolved in them.

In general, it may be said that a nucleus promotes condensation of vapor upon itself by introducing locally into an otherwise uniform vapor a sudden pressure gradient, owing to the diminished pressure of the portion of the vapor that is directly in contact with the nucleus. This diminished pressure is brought about by the nucleus itself—either because of its curvature, or because it possesses chemical affinity for the vapor, or because it is electrically charged.

To this pressure gradient, there corresponds a concentration gradient. Such a localized concentration gradient produces what is virtually a free surface—a kind of interface, separating regions of vapor of different concentrations from one another—so that the forces of intermolecular attraction, which, in the homogeneous vapor, may be considered to act uniformly in all directions, now become oriented about certain centers, and produce surface tension and the beginning of localized surfaces in the vapor.

The temperature of condensation.—In describing the condensation of water vapor, it has been assumed that the temperature of the system remained above the freezing point throughout the process.

If the condensation of water vapor be carried out at temperatures below zero, a cloud of ice crystals is produced.[3] If, on the other hand, a cloud of liquid particles, formed by the condensation of water vapor at temperatures above 0° C., be cooled below zero in the complete absence of the solid (ice) phase, the particles can be subcooled to temperatures as low as — 30° C. without solidifying. When such subcooled droplets come into contact with a solid surface, they solidify, the surface becoming coated with an ice scale.

In this respect, water vapor is typical of a large number of substances that condense to form solid-gas or liquid-gas aerosols, according to whether the temperature of condensation is below or above the melting point of the disperse phase.

We have seen that, when a vapor condenses in the presence of a chemically indifferent gas, the character (particularly the degree of dispersion) of the resulting condensate can vary widely, depending upon the nature of the particular gas that is used. This appears to be due to differences in the degree of natural ionization that is exhibited by different gases, with corresponding differences in the number of condensation nuclei that are available. The gaseous dispersion medium can also affect the degree of dispersion that is obtained in a given condensation, by becoming adsorbed upon the surfaces of the newly formed particles, so that their further growth is inhibited and an aerosol possessing a high degree of dispersion, and also a high degree of stability, is produced.

The study of the condensation of metal vapors in vacuo and in various gases shows that the degree of dispersion of the condensate is higher, the greater the pressure and density of the gas. The more numerous the gas molecules and the heavier they are, the more likely they are to become adsorbed upon the surface of the newly formed particles.*

Other condensation processes.—Aerosols are often produced by methods in which condensation forms the last and least obvious stage of a more complex process.

When two gases—*e.g.*, NH_3 and HCl—interact, one or both of the products of the reaction may possess a very much lower vapor pressure than either of the reactants. The system will thus become supersaturated with respect to the relatively non-volatile resultant, so that a part of it will condense to form a disperse system. Since gases are molecularly disperse systems, we may assume that, in the first stages of the reaction, the resultant will be produced in a molecularly disperse condition. This high initial degree of dispersion will rapidly become lower, owing to the growth of these particles, either by the condensation of further quantities of vapor upon them or by the formation of aggregates by coalescence or flocculation.

The extent to which the initially high degree of dispersion of such a system diminishes, and the rate at which this occurs, will depend, *cæteris paribus*, upon the initial concentration of the reacting gases, and the difference between the amount of the resultant that is produced per unit volume in the reaction, and the actual concentration at which it can exist in the vapor phase.

If the gases react immediately they are brought into contact with one another—*e.g.*, NH_3 and HCl—then the formation and precipitation of the reaction product occurs at the surface of contact of the two gases, and only spreads as the gases mingle (surface condensation). This form of reaction necessarily produces an aerosol of a lower and more uneven degree of dispersion.

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* The kinetic motion is less with heavier particles. J. A.

If, however, the gases can be mixed completely before they react—for example, photochemical reactions, in which reaction is catalyzed by light (*e.g.*, H_2S and SO_2)—then precipitation takes place in and from a homogeneous medium, and a uniform aerosol results (volume condensation).

Other typical condensation processes may be summarized as follows:

(a) A salt, introduced into a Bunsen flame, vaporizes in the hot gases of the flame. The mixture of hot gases and salt vapor is cooled by mixing with the surrounding air, and the vapor is condensed. Similarly, when an arc is formed between two metal electrodes, metal vapor is formed, and, mixing with the surrounding air or gas, becomes diluted and cooled, and condenses in the form of smoke. The character of the aerosol produced can be modified, according to the nature and pressure of the gas that is used.

(b) When a volatile solid—*e.g.*, NH_4Cl—is heated sufficiently, it volatilizes; the vapor mixes with cold air, and condenses to form a smoke.

(c) When a current of air passes over or through a hot solid or liquid that is only slightly volatile, the air becomes heated and saturated with vapor at the temperature of contact. A part of this vapor is precipitated as the air passes from the heated zone and cools. Such bodies as anthracene, acetanilide, diphenylamine, orthophthalic acid, paraffin wax, readily produce highly disperse smokes by this method. Other substances, such as benzyl benzoate, or clean mercury, produce either a coarse cloud or no detectable smoke.

(d) A hygroscopic substance does not fume in moist air at a given temperature—for example, the ordinary room temperature—unless either it, or one of the products of hydrolysis, possesses a considerable vapor tension at the given temperature. HCl, Al_2Cl_6, $SnCl_4$, fume in moist air at the ordinary temperature, but $CaCl_2$ and H_2SO_4 do not. The fume is produced by the condensation of atmospheric water vapor upon the hygroscopic vapor molecules.

THE DEGREE OF DISPERSION OF AEROSOLS

When an aerosol is formed by the condensation of a vapor, its degree of dispersion at the moment of formation is exceedingly high, closely approaching that of the vapor itself. This primary degree of dispersion depends upon the concentration of the initial gas or vapor, the degree of supersaturation from which it condensed, the character of any non-condensing gas that is present, the extent to which the gas is nucleated and the character of these nuclei (Barus). It has been shown that a high primary degree of dispersion is produced when a slightly supersaturated vapor condenses in a dense gas at high pressure and that contains a large number of suitable nuclei. This primary degree of dispersion gradually diminishes as the particles collide with one another and coalesce. The rate at which this change takes place depends primarily upon the collision frequency of the particles. For a given degree of dispersion, this will clearly be proportional to the number of the particles that are present in unit volume, and the pressure and temperature of the gas. The degradation of the aerosol will be hastened by increasing the number of particles per unit volume—*i.e.*, the concentration—or by raising the temperature or reducing the pressure of the gas. As the high primary degree of dispersion is succeeded by the lower secondary degree of dispersion, the particles will become less numerous, and will move more and more sluggishly. Consequently, the aerosol, as it becomes coarser, gradually destroys, or, at any rate, diminishes, the very forces that promote its degradation. Ultimately, a point is reached at which the particles are relatively so few or so sluggish in their movements that the chance of collision, and, therefore, of coalescence, occurring is exceedingly small. Then, a relatively stable secondary degree of dispersion is attained, and further change occurs comparatively slowly.

The degree of dispersion of aerosols has been determined:

(a) By observing with an ultramicroscope the amplitude of the Brownian motion (A), and substituting in the general equation

$$r = \frac{RT}{N} \cdot \frac{t}{3\pi\eta A^2}. \tag{3}$$

Since r varies as the *square* of A, the accuracy of the method is not very high.

(b) By observing the velocity (V) that is imparted to a charged particle by an electric field of X volts per centimeter.

$$V = \frac{Xe}{6\pi\eta r}, \tag{4}$$

where e is the charge on the particle.

$$\text{Putting} \quad e = 1.59 \times 10^{-20},$$
$$r = \frac{4.65 \times 10^{-10}}{V},$$

The most satisfactory application of this method is that devised by Wells and Gerke.[4] They photographed the regular zigzag paths that are traced by the particles under the simultaneous influence of convection currents and an alternating electric field. The amplitude of these oscillations is an accurate measure of the distance that is traced by the corresponding particle in a definite, small interval of time under the influence of the known electrical force. A great advantage of this method is that particles of different sizes can be measured simultaneously. Also, it is possible in this way to determine the range and distribution of the sizes of the particles forming a given aerosol at a given moment of time. Individual particles have been weighed by applying a vertical electrical force to the particle, thus imparting to it a velocity greatly in excess of either its gravitational or Brownian movements. The mass of the particle is obtained by applying Stokes' law to the difference between the observed upward and downward velocities of the particle.

(c) By determining the concentration of the disperse phase and dividing it by the number of particles, previously determined by direct observation with an ultramicroscope.[5] This gives an accurate estimate of the average mass of a particle, and, assuming its density to be identical with that of the undispersed substance, it is possible to obtain a value for the radius of the particle. By this method, it is possible, also, to trace the gradual growth of the particles of flocculation or coalescence.

In the following Tables, I, II, and III, are shown, at different intervals of time, (I) the number of particles, (II) the concentration of the disperse phase, and (III) the average mass of the particles, of a zinc oxide smoke.[5]

TABLE I

Zinc Oxide Cloud. Number Curve

Time h.	Time m.	Particles per c.c.	Time h.	Time m.	Particles per c.c.	Time h.	Time m.	Particles per c.c.
0	4	4.54×10^6	1	51	1.68×10^6	2	47	0.88×10^6
0	26	2.99	1	53	1.42	2	49	0.77
0	29	2.89	1	55	1.31	2	51	0.69
0	51	2.09	1	58	1.59	4	7	0.56
0	53	2.25	2	28	0.91	4	10	0.48
1	21	1.68	2	33	0.81	4	16	0.56
1	24	1.65	2	34	0.92			

TABLE II

Zinc Oxide Cloud. Microbalance Curve

Time h.	Time m.	Weight (Mgrm. per Litre)	Time h.	Time m.	Weight (Mgrm. per Litre)
0	10	0.0172	2	46	0.0124
0	35	0.0187	4	23	0.0081
1	3	0.0171	4	36	0.0079
1	33	0.0141	4	50	0.0076
2	11	0.0147			

TABLE III

Table Showing the Average Weight of a Particle at Different Periods

Time h.	Time m.	Average Weight per Particle, Grm.	Time h.	Time m.	Average Weight per Particle, Grm.
0	4	3.62×10^{-15}	3	0	15.1×10^{-15}
0	30	6.60	3	30	16.4
1	0	8.37	4	0	16.9
1	30	9.82	4	30	16.9
2	0	11.7	5	0	16.8
2	30	13.6			

(d) By observing the optical properties of the system. These methods are fully described elsewhere.

The Movements of the Particles

The particles of an aerosol move under the influence of:

(a) forces which originate independently of the gas—*e.g.,* gravitation, centrifugal action, an electrical field;

(b) the molecular bombardment of the gas itself—that is, Brownian motion.

The same forces, of course, are also exerted upon the gas molecules themselves, but, owing to their much smaller mass, with very different results.

It will be convenient at first to confine our attention to one external force—gravitation—remembering that, in its influence upon the motion of the particles, it is typical of all forces that operate externally to the gas.

The velocity with which small spherical particles move through a uniformly viscous fluid (liquid or gas) under the influence of an external force—*e.g.,* gravity, or, if the particles be charged, an electrical field—will be equal to $\frac{F}{K}$, where F is the strength of the force, and K is the frictional resistance encountered by the particle when passing through the gas.[6] For particles suspended in air or any other fluid, the force due to gravity is equal to $\frac{4}{3}\pi r^3(\rho -$

$\rho')g$, where ρ is the density of the particles, and ρ' is that of the fluid. The resistance $K = 6\pi\eta rv$, where η is the viscosity of the gas, r the radius of the particle, and v its velocity.

The particle falls with increasing velocity, and, since K, the resistance with which it meets, increases with the velocity, K ultimately becomes equal to F; the particle then falls with constant velocity V.

At this point—

$$6\pi\eta rv = \frac{4}{3}\pi r^3(\rho - \rho')g, \tag{5}$$

so that v, the ultimate constant velocity of the particle, will be equal to

$$\frac{2}{9}r^2\frac{(\rho - \rho')g}{\eta}. \tag{6}$$

For particles of a given substance falling in a given gas, $(\rho - \rho')$ and η will have constant values, so that V will be directly proportional to r^2.

For cloud droplets sinking in air, $(\rho - \rho')$ can be regarded as equal to 1, $\eta = 1.81 \times 10^{-4}$ cgs. units, so that

$$V = 12 \times 10^{-5} \times r^2 \text{ cm. per second.}$$

The relation r and V is shown in Table IV.

TABLE IV

Radius of Droplet, (r) Cm.	Rate of Fall, (V) Cm. per Second
10^{-2}	$120 = 4.320$ metres per hour
10^{-3}	$1.2 = 43.2$ metres per hour
10^{-4}	$12 \times 10^{-3} = 43.2$ cms. per hour
10^{-5}	$12 \times 10^{-5} = 4.32$ mms. per hour

Since both η and ρ' possess smaller values for gases than for liquids, the limiting velocity with which a given particle falls in a gas will be much greater than in a liquid. Thus, spherical particles of unit density and radius 0.4 μ settle in air at normal temperatures and pressures at the rate of 0.003 cm. per second. In water, they would only settle 0.003 cm. in three days.

Non-spherical particles fall in the position in which they will encounter maximum resistance. Thus, a flat plate will fall in a horizontal position.

Since the limiting velocity is inversely proportional to the viscosity of the gas, a given particle will fall approximately twice as quickly in hydrogen or water vapor ($\eta = 0.93$ and 0.971×10^{-4}) as in air ($\eta = 1.9 \times 10^{-4}$).

The apparent density of a particle may differ considerably from the normal density of the substance, owing to the presence of a film of adsorbed gas upon it. It would then fall with diminished velocity.

The mean free path of gas molecules at normal temperature and pressure is 10^{-5} cm. Consequently, particles of diameter less than 10^{-5} cm. will tend to slip between the molecules of the gas, so that the resistance exerted by the gas will be variable and will possess a relatively lower average value. It has been shown by Cunningham and Millikan[7] that, for such particles,

$$V = V'\left(1 + K\frac{\lambda}{r}\right), \tag{7}$$

where V is the true velocity and V' the velocity according to Stokes' law, λ is the length of the mean free path of the gas molecules, and r is the radius of the particle. K is a constant, approximately equal to 0.86.

In liquids, the length of the mean free path of the molecules is of the order of the diameter of the molecules themselves. Consequently, this correction only becomes necessary for particles approaching molecular dimensions. In gases, the length of the mean free path of the molecules can be varied over a wide range by altering the pressure of the gas. In this way, the fall of relatively large particles can be observed microscopically under conditions which simulate those that obtain in more highly disperse colloidal systems.

Millikan[8] investigated the behavior of charged oil droplets suspended in a gas, and exposed to the action of a vertical electric field.* By an ingenious contrivance, individual oil droplets could be introduced into an observation chamber formed between two parallel horizontal electrodes. The oil was sprayed in the form of a fine mist into a chamber situated above the upper electrode. The oil particles were found to be strongly charged by the spraying process. Individual particles found their way into the observation chamber through a pinhole in the upper electrode. By applying a force of some thousands of volts, the gravitational force upon a given particle could be balanced, so that, after falling through a given distance under gravity, the particle could be brought back to its original position and the fall repeated as many times as desired. It was thus possible to observe accurately the rate of fall of a given particle. By diminishing the pressure of the surrounding gas, the rate of fall of the particle for different values of λ could be determined.

The relation between V and V' for small oil drops, calculated from Millikan's observations, is shown in the following table:

TABLE V

Stokes's Law	Stokes-Cunningham Law
1×10^{-4}	1.14×10^{-4}
1×10^{-5}	2.57×10^{-5}
1×10^{-6}	4.50×10^{-6}
1×10^{-7}	17.00×10^{-7}

Brownian Movement.

As the size of the particles becomes less than 10^{-5} cm., the molecular bombardment to which they are subjected by the gas molecules becomes more irregular and more effective. Instead of pursuing a direct course through the gas, undisturbed except by convection currents or other general movements of the gas itself, the particle now staggers about the gas in response to the successive impacts of the gas molecules. This Brownian motion is, of course, superimposed upon that due to gravity. As the size of the particle further diminishes, the influence of gravity becomes less, and that of molecular impact greater, until the path of the particle resembles that described by a football in play, but on a playing-field in three dimensions!

In Table VI, the velocity acquired by silver particles of different sizes under the influence (a) of gravitation, and (b) of molecular impact, are compared.[9]

Ehrenhaft found that particles larger than the mean free spaces of the gas (1×10^{-5} cm.) fell in a zigzag line, the velocity due to gravitation being greater than that due to molecular impacts. With small particles down to 1×10^{-7} cm. (near the limit of visibility in the ultramicroscope), the velocity due to molecular impacts is greater than that due to gravitation. These particles remain in active Brownian motion in the gas, the motion being increasingly rapid the smaller the particles.

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* See paper by R. A. Millikan, this volume, p. 174. J. A.

TABLE VI

Velocity Due to Gravitation	Velocity Due to Molecular Impacts	Radius of Particles
12×10^{-8} cm./sec.	6.3×10^{-3} cm./sec.	1×10^{-7} cm.
3×10^{-6} " "	2.8×10^{-3} " "	5×10^{-7} "
12×10^{-6} " "	2.0×10^{-3} " "	1×10^{-6} "
3×10^{-4} " "	8.9×10^{-4} " "	5×10^{-6} "
12×10^{-4} " "	6.3×10^{-4} " "	1×10^{-5} "
3×10^{-2} " "	2.8×10^{-4} " "	5×10^{-5} "
12×10^{-2} " "	2.0×10^{-4} " "	1×10^{-4} "

The mean kinetic energy of any particle in Brownian motion is equal to that of the molecules of the fluid in which the particle is suspended. At a given temperature, the kinetic energy of a particle of mass M, and velocity V, $= K$.

$$\begin{aligned} \tfrac{1}{2}MV^2 &= K \\ &= \tfrac{1}{2}mv^2, \end{aligned}$$

where K is a constant at a given temperature, and m and v are the mass and velocity, respectively, of the gas molecule. That is to say, the velocity of Brownian motion of any particle is inversely proportional to the square root of its mass.

At a given temperature, this velocity is the same for any particle of given mass M, whether it be suspended in a gas or a liquid.

At normal temperature and pressure, the mean free path of a molecule of a gas is some hundreds of times as long as that of a molecule of a liquid. Consequently, the length of the mean free path that is described by a particle between two consecutive impacts (the amplitude of Brownian motion) is very much greater in a gas than in a liquid.

Consequently, the distance that a given particle travels in a given time in a gas is very much longer than that described by a similar particle in a liquid at the same temperature. The general effect of the greater amplitude of Brownian motion in gases, etc., is to delay settling and promote diffusion.

Diffusion.

A direct result of the Brownian motion of the particles is their ability to diffuse throughout the dispersion medium.

The rate of diffusion (D) of smoke particles is related to the amplitude (A) of their Brownian motion by the expression[10] $D = \frac{1}{2}A^2/t$. Combining this with equation (3), we get—

$$D = \frac{1}{2}\frac{A^2}{t}, \tag{8}$$

$$= \frac{1}{2}\frac{RT}{N} \cdot \frac{1}{3\pi\eta r} \tag{9}$$

For a given dispersion medium and at a given temperature, $D = \frac{k}{r}$,—*i.e.*, the smaller the particle, the more rapidly it will diffuse.

From this, we see that the finest smoke particles diffuse much more slowly than the molecules of a gas. It is, therefore, very much more difficult to filter smoke particles from a gas than to effect the removal of a gaseous constituent of a gas mixture by passing it through an adsorbent. During the passage of a gas-smoke mixture through a filter, only a small proportion of the slowly diffusing smoke particles come into contact with the filtering surfaces, whereas practically all the molecules of a gas will do so. This difference between the rate of diffusion of smoke and gas was a factor of first importance in designing gas masks during the War.

When a volume of gas containing smoke is discharged into the atmosphere —*e.g.*, during a gas attack—the smoke reinforces the gas and holds it together, so that it retains its identity for a long time and can travel almost intact for a considerable distance, whereas a gas cloud alone would speedily diffuse in all directions and become dissipated.

Since $D = \frac{1}{2}\frac{A^2}{t}$, it follows that particles of any given size will diffuse very much more rapidly in a gas than in a liquid. In neither case, however, is the rate of diffusion sufficiently great sensibly to affect the stability of the system.

Thermal Precipitation.

When an electrically neutral particle, too large to exhibit Brownian motion, is suspended in a thermally and electrically uniform gas, the molecular bombardment will be uniform in all directions, and will produce no displacement of the particle. If, however, a thermal gradient be set up in the gas—for example, by introducing a hot rod into it—the gas molecules in the neighborhood of the rod become "warmed" and move more energetically than those more remote. Any such particle, therefore, suspended in the gas in the immediate vicinity of the rod, will be repelled from it. Smaller particles in Brownian motion will pursue a zigzag path away from the hot rod. The rod thus becomes surrounded by a region of warm, dust-free air, streaming upwards.[11]

A cold rod gives rise to a down-streaming current of more dusty air. In this case, the dust is deposited upon the rod as the warm, dusty air streams downward over its cold surface.

Solid particles present in flames are deposited more easily upon a cold surface than upon a hot surface. A flame of burning magnesium will deposit magnesium oxide soot upon a cold flask held in the flame, but not upon a similar flask containing boiling water.

In rooms that are heated by direct radiation—*e.g.*, by an open fire—the walls and furniture of the room are warmer than the air. Consequently, the dust in the air remains in suspension. In rooms that are heated by convection —*e.g.*, by steam-pipes or hot-water "radiators"—the air is warmer than the objects in the room, and, therefore, deposits the suspended dust upon them. This dust deposition is very pronounced upon walls and ceilings above a radiator or lamp, and more particularly on those portions of the ceiling that are cooled by contact with air pockets between the rafters.

Tolman has shown that tobacco smoke, passed between two concentric tubes maintained at a temperature difference of from 50° to 80° C., will be quantitatively deposited upon the cold surface.

The Stability of Aerosols

The stability of aerosols is commonly comparable with that of disperse systems in liquids. Atmospheric clouds and mists may persist for days in still air without being flocculated. Smoke will travel miles along flues without appreciable change; it is only dissipated by becoming mixed with large volumes of air.

Whytlaw Gray,[12] working with smokes of NH_4Cl, CuO, ZnO, and CdO, contained in a closed vessel, found that their life history could be separated into three periods:

(a) An unstable period, lasting for five hours or more, during which the *number* of particles rapidly decreased with time, due to *flocculation*. The average size of the particles gradually increased.

(b) A stable period, in which the number of particles diminished slowly, due to *settling*. This stage lasted in some cases for 24 hours or more, even in a chamber of only 1 cubic meter capacity.

(c) These two stages overlap, to produce an intermediate stage in which flocculation and settling both operate.

We have seen that the stability of any aerosol depends primarily upon the degree of dispersion. The particles of highly disperse systems—smokes—tend, on account of their vigorous Brownian movement and the large number of them that are present per unit volume, to flocculate, until, owing to their increasing mass, their Brownian motion becomes so sluggish that further collisions become too infrequent to produce appreciable flocculation. The resulting aggregates then settle slowly and persistently under the influence of gravitation.

Clearly, the stability of an aerosol will be enhanced if the process of flocculation is arrested. This occurs when the particles are surrounded by films of adsorbed gas, or when the particles are all charged electrically with the same sign.

Protection by Adsorbed Gas.

Gases, being less "condensed" than liquids, are more readily adsorbed. The copious adsorption of gases by charcoal and by silica gel is a special instance of the general experience that a great variety of substances in a finely divided condition adsorb gases.

When an adsorbent is brought into contact with a mixture of gases—*e.g.*, the atmosphere—the most compressible gas (in this case, oxygen) is generally adsorbed the most strongly. Beyersdorfer[13] has shown that, if 200 grs. lump sugar be ground up in a gas-tight mill for 24 hours, the pressure of the air in the mill is reduced to 23 mm., owing to the adsorption of air. The presence of adsorbed oxygen upon combustible dusts—*e.g.*, sugar—is an important contributing factor in the production of dust explosions. The blue smoke from a brass foundry contains particles of zinc oxide dispersed in a mixture containing considerable amounts of SO_2 and water. It is a very stable smoke, passing unchanged through wet coke scrubbers and other forms of washers. This is to be attributed to the protective effect of adsorbed gas. When the smoke is collected by filtration through woollen filters, the ZnO powder is exceedingly light (sp. gr. 0.2), and mobile. It flows and surges like a limpid liquid. In the same way, pulverized coal, rock dust (SiO_2), and powders such as lampblack, contain relatively enormous volumes of adsorbed gas. It would be a matter of great interest and importance to investigate the adsorption of different gases by various finely divided solids, either by grinding the material in the gas contained in a gas-tight mill and analyzing the residual gas, or by heating the mixture of powder and adsorbed gas and determining the volume and composition of the gas that is set free.

In the same way, finely divided *liquid* particles—*e.g.*, H_2SO_4 mist—become protected by adsorbed gas.

The presence of adsorbed gas upon the particles of an aerosol interferes in some way with the precipitation (ionization) of the particles by a corona discharge. Such particles behave as though the gaseous ions that come into contact with them were unable to adhere.

By choosing as the dispersion medium a gas that will be strongly adsorbed by the particles of the disperse phase, it should be possible in general to prepare aerosols of maximum stability. In general, a gas is adsorbed more readily, the higher its boiling point. For a given adsorbent and a given gas, the amount of adsorption is greater the higher the pressure of the gas and the lower the temperature.

In reducing substances to a finely divided condition by grinding or spraying, the nature of the gas in which the preparation is carried out is probably a matter of first importance.

In many industrial processes, the reverse process—that of removing such films of adsorbed gas, in order that flocculation or precipitation may occur—is frequently an urgently important matter.* It has been shown in some cases that such films can be displaced, and flocculation assisted, by changing the composition of the dispersion medium—for example, by the addition of water vapor. In some cases, particularly with liquid particles, the film can be displaced by a sufficiently intense mechanical impact.

Unquestionably, a great deal of interesting and important work has yet to be done before we can apply this phenomenon successfully to the treatment of smokes.

Electrical Charges.

When a freshly formed smoke—*e.g.*, tobacco smoke—is placed between two charged plates and examined under a microscope, some of the particles will be seen to be positively charged, some negatively, other neutral. When oppositely charged particles, or charged and uncharged particles, exist in the same aerosol, they will naturally attract one another and thus promote flocculation, so that the degree of dispersion of the system will rapidly diminish, and it will reach a final degree of dispersion at which settling will set in. When, however, the particles are all charged and with the same sign, they will naturally repel one another and so inhibit flocculation. Such a system will possess a considerably enhanced stability.

An aerosol in which the particles are similarly charged is formed when substances like petroleum or sugar are dispersed mechanically in air, owing to the generation of electricity by friction between the particles and the spray-nozzle or mill at the moment of formation and separation. The accumulation in the air of inflammable dust, carrying static electrical charges, has been shown by Beyersdorfer to be a direct cause of dust explosions.

Flocculation can be induced in such electrically charged systems by introducing oppositely charged particles. Atmospheric clouds have been dispersed by scattering charged sand upon them.

Aerosols differ from disperse systems in liquids: (1) in the greater extent to which the dispersion medium is adsorbed by the disperse phase, and (2) in the presence simultaneously of particles charged with opposite signs.

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* Gases adsorbed by B_2O_3 powder delay its solution and often form bubbles that carry little lumps to the surface. If wet with alcohol, the gas is displaced, and solution in hot water is rapid. J. A.

Flocculation.

When crystalline particles—*i.e.*, possessing definite polarity—free from adsorbed gas, come into contact, they will tend to form aggregates possessing a definite crystalline form. Amorphous particles, similarly, will produce aggregates of no definite form.

Particles that are surrounded by a layer of adsorbed gas—*e.g.*, one molecule thick—will still be able to attract one another, but will be unable to coalesce, unless the force with which they attract one another is sufficient to displace the gas film at the point of contact. Such particles will form fluffy aggregates, in which the individual particles will be separated from one another by the layers of gas—*e.g.*, zinc oxide. If the force of attraction exerted by the particles is definitely polar in character, they will only be able to attract each other in certain directions. This will inevitably lead to the formation of string-like aggregates, much in the way that iron filings arrange themselves along a line of magnetic force. Such string-like aggregates were observed by Whytlaw Gray to be formed by particles of CdO and ZnO. Gradually, these thread-like aggregates unite to form a complex network, comparable to the gel that is formed by the coagulation of a sol. Such network aggregates may conveniently be regarded as aerogels. Familiar instances are the flocks of zinc oxide that are formed by the combustion of zinc vapor.

Tolman[14] has shown that the stability of an aerosol is rapidly destroyed by stirring or agitation, because the particles are brought into contact with the walls of the containing vessel, to which they adhere.

He also found that, for a given degree of dispersion, the stability was diminished when the concentration was increased, for the particles then collided more frequently with each other and with the walls of the container.

The Physical and Chemical Behavior of Aerosols

An aerosol differs from other disperse systems in the great disparity that exists between the density and structure of the disperse phase and of the dispersion medium. The droplets of water in a cloud, for example, are more than eight hundred times as dense as the air in which they are suspended.

A gas possesses a more open structure, and, therefore, a much lower viscosity, than a liquid. Its molecules move freely along paths that are much longer than those that obtain in liquids; consequently, a particle that is suspended in a gas can move through the gas under the influence of an external force—*e.g.*, gravity—much more freely than through a liquid. Also, Brownian motion possesses a greater amplitude, and can be exhibited by larger particles than in a liquid, particularly when the mean free path of the gas molecules is increased further by reducing the pressure of the gas.

The conditions under which physical equilibrium can exist between the two phases of any disperse system—and, therefore, the stability of the system—cannot be completely defined by the phase rule, owing to the effect of (a) the curvature of the surfaces of the particles, (b) the presence of adsorbed films upon the particles, or (c) the presence of electrical charges upon the particles. These effects are more marked in aerosols again, because of the relatively low density and open structure of the dispersion medium.

The character of a disperse system may be very unlike that of either of its constituents: a solid or liquid substance frequently exhibits profoundly different characteristics when it is reduced to a fine state of division. The acute curvature of the particles increases its physical activity, so that it melts or dissolves or volatilizes more readily, and the enormously increased specific surface results in a greatly intensified chemical activity.

The physical properties of a body of gas are greatly modified by the presence in it of a highly dispersed solid or liquid:

(a) *It is denser and less mobile.*—The presence of a large number of particles that diffuse very slowly or not at all increases the density and checks the diffusion of the gas. A given volume of an aerosol will persist for a longer time, and will move bodily through the atmosphere, for example, for much greater distances, before being disintegrated by diffusion. Smoke was used in this way to "carry" gas during the war.

(b) *It is more sensitive to visible and thermal radiation.*—A gas is almost completely transparent to optical or thermal radiation. An aerosol is less transparent, and will adsorb or reflect radiation or will re-radiate it to an extent that will depend upon the specific optical properties of the dispersed substance, and also upon its concentration and degree of dispersion.

Dusty air is more sensitive to thermal changes than dust-free air. It is warmed more rapidly by sunshine, owing to the adsorption of heat by the dust particles. It cools more rapidly when the sun goes down, because the dust particles radiate heat towards the sky. The production of smoke screens in warfare, and the prevention of frost in orchards by the use of "smudge pots," depend upon the capacity of smoke to adsorb light and reflect heat, respectively.* A flame is an aerosol. When it is luminous, it is because of the radiation that is emitted by the solid particles—generally, of carbon—that are dispersed throughout the hot gases. An almost completely gaseous flame—*e.g.*, a Bunsen burner flame—is practically non-luminous and radiates very little heat.

(c) *An aerosol has a greater specific heat.*—The increased specific heat of furnace gases, due to the presence of particles of smoke and ore, assumes importance in some metallurgical calculations.

(d) *Its electrical character is altered.*—The degree of ionization of the gas is diminished at first, as the charges are rapidly transferred from the gas molecules to the particles of the disperse phase, where they either neutralize one another, or persist, to form slow-moving smoke ions of relatively large mass. After this, the degree of ionization will diminish very slowly, since the frequency of impact between these sluggish smoke ions is relatively very low.

The conductivity of the gas is lowered, since the rate of re-combination of the more rapidly moving gaseous ions is increased, and the more stable smoke ions possess but feeble mobility. It is possible to watch for a comparatively long time the movements of these relatively stable smoke ions in an electrical field, and thus to picture something of the character of the incredibly swifter movements of gaseous ions themselves.

A charged particle suspended in a gas can be induced to move in any given direction by applying a suitable electrostatic force. It is possible to make the particle move vertically upwards with a force that just balances the force due to gravity, or that may be greater or less than it. By this means, the movements of particles in a gas under definite conditions of temperature and pressure can be controlled, and, since the movement due to the electrostatic field is proportional to the charge carried by the particle, while the movement due to gravity is proportional to the mass of the particle, it is possible, by choosing suitable conditions, to determine either (a) the amount of charge carried by a given particle, (b) the mass of a given particle, or (c) the magnitude of its Brownian movement.

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* See J. Alexander, *Science;* "Colloid Chemistry" 2nd ed., p. 67. Brick works in northern Sweden prevent freezing on cold nights of spring and fall by causing their peat fires to smoke from lack of sufficient air. J. A.

INDUSTRIAL AEROSOLS

The production of an aerosol is a familiar consequence of many industrial operations. The disperse medium of such an aerosol may be either the atmosphere (*e.g.*, the dusty atmosphere of mines and mills), flue gases from a furnace (*e.g.*, metallurgical fume and sulphuric acid mist), or fuel gases (*e.g.*, blast furnace gas and producer gas).

It is convenient to distinguish between three kinds of industrial aerosols according to the size of the suspended particles (the degree of dispersion).

(a) *Dusts,* in which the particles are larger than 10^{-3} cm. diameter. Such particles settle in still air with increasing velocity. They do not diffuse.

(b) *Clouds,* the particles of which range in diameter from 10^{-3} to 10^{-5} cm. Such particles settle in still air at a constant velocity, depending upon their size, according to Stokes' law. They, also, do not diffuse.

(c) *Smokes,* the particles of which range from 10^{-5} to 10^{-7} cm. diameter. Such particles are in active Brownian motion, and diffuse fairly rapidly. They do not settle at all in still air.

The degree of dispersion of a number of industrial dusts, clouds and smokes is shown in Table VII.

TABLE VII

Substance	Diameter of Particles, Cm.
Milk powder (by evaporation of fine spray)	1.4×10^{-2} to 0.7×10^{-2}
Fine powder (300 mesh)—*e.g.*, cement	1.0×10^{-2} to 0.7×10^{-2}
Smelter fume	1.0×10^{-2} to 1.0×10^{-5}
Atmospheric fog particles	1.4×10^{-3} to 3.5×10^{-3}
Cement kiln flue dust..............................	6.0×10^{-3} to 0.8×10^{-3}
H_2SO_4 mist from concentrators....................	1.1×10^{-3} to 1.6×10^{-4}
NH_4Cl fume	1.0×10^{-4} to 1.0×10^{-5}
Oil smoke	1.0×10^{-4} to 5.0×10^{-6}
Rosin smoke	1.0×10^{-4} to 1.0×10^{-6}
Tobacco smoke	1.5×10^{-5} to 1.0×10^{-6}

These industrially important aerosols are formed either—

(1) By the condensation of vapors of metals (mercury, silver, copper, lead, zinc, arsenic, antimony), or of metallic compounds (oxides, sulphates, chlorides), that are formed in the hottest parts of the smelting furnace, and condense in the fume after it leaves the furnace, or by the condensation of non-metallic vapors—for example, of tar vapors in producer gas.

(2) By chemical action between metallic vapors and the furnace gases (oxygen, chlorine, sulphur trioxide), to form compounds that are not volatile at the temperature of the furnace—*e.g.*, SnO_2 from a tin-smelting furnace, or ZnO fume from a brass foundry—or that are volatile at the furnace temperature, but condense as the fume passes away and cools—*e.g.*, chloride vapors from a chloridizing roast, and As_4O_6 from an oxidizing roast.

(3) By mechanical disintegration and dispersion of solid or liquid substances—*e.g.*, ore dust carried over from a furnace; the dust in the air of grinding mills and mines.

In many cases, substances are manufactured in powder form by being dispersed in a gas and subsequently collected—for example, milk powder, carbon black, zinc dust.

For a variety of reasons, it is frequently necessary either to prevent the formation of such aerosols, or, once they are formed, to separate the particles of the disperse phase from the dispersion medium. Thus:

(a) *The dust may be dangerous to the workers.*—It may be directly injurious—*e.g.*, some dusts are directly poisonous when they are inhaled by the workers. In many grinding mills and packing rooms, the dust—*e.g.*, siliceous material—when inhaled by the workers, would be directly harmful to their lungs.

It may be explosive, and at any moment become ignited, with disastrous consequences. In many mills in which combustible substances such as flour, starch, sugar, coal, are ground, fine particles are caught up into the air, and, unless the air is circulated and filtered continually, the concentration of suspended dust may reach the explosive limit.

(b) *It may be obnoxious.*—Smelter fumes and acid fumes containing dust and acid particles may constitute a serious public nuisance. In most countries, stringent regulations are in force to restrict the content of the disperse phase to within a very small limit.

(c) *It may impair the quality of the gas* (*e.g.*, producer gas or blast-furnace gas that is to be used in gas engines), *or of some product that is made in contact with the gas.*—There are many manufacturing processes—*e.g.*, textiles, photographic films, gas mantles—that must be carried out in dust-free air. Air compressors and air-cooled turbo-generators must be supplied with cool, dust-free air; otherwise, dust collects in the air passages or on the windings, impairing the cooling efficiency and causing a risk of breakdown due to possible short-circuiting.

(d) *It may be too valuable to waste.*—Smelter fumes, particles from copper, silver, tin, arsenic and mercury furnaces, contain suspended matter worth many times more than the cost of recovery.

Sometimes it is possible to prevent the distribution of dust in the atmosphere in the neighborhood of grinding mills by keeping the work wet. In most cases, however, it is not possible to prevent the formation of an aerosol, and the particles of the disperse phase have to be removed by some means from the gas in which they are suspended.

The method to be adopted for the purification of a particular metallurgical smoke will depend very much upon the character of the gases, their temperature, volume and composition, the nature of the suspended matter, its physical and chemical composition and economic value, and the immediate destination of the purified gases, whether to be used for power purposes or to be discharged into the air.

All smoke-treating or dust-recovery processes should be continuous in action, and should offer as little resistance as possible to the passage of the smoke. One of the inherent difficulties associated with the filtration of smelter smoke is the enormous volume of smoke that has to be treated; frequently as much as a million cubic feet of smoke has to be treated per minute, from twenty to thirty tons of material being recovered per day. It is a matter of first importance, therefore, that any process of filtration or condensation be rapid; otherwise, the dimensions of the plant will be prohibitively large.

Separation by Settling.

With relatively coarse particles, advantage is taken of their readiness to settle out of the gas by gravity. The efficiency of any settling process rapidly becomes less as the degree of dispersion increases; it is only of practical importance where the diameter of the dust particles exceeds 10^{-3} cm. The efficiency of any settling process is increased:

(1) By retarding the rate at which the gas is travelling, so that the particle remains for a longer time in the settling chamber.

(2) By reducing the distance through which the particles fall, generally by dividing the settling chamber into a number of superimposed, shallow, horizontal compartments by means of horizontal partitions spaced a few inches apart.

(3) By submitting the fume to centrifugal force, either by causing it to enter tangentially a fixed cylindrical vessel—the so-called "cyclone" dust-catcher—or by introducing the fume actually into a rapidly rotating cylindrical vessel. In many cases the fume is subjected repeatedly to centrifugal force by suddenly changing its direction, as, for example, by causing it to travel along a zigzag flue. A similar sudden change of direction is obtained when the fume is passed through a series of parallel perforated plates, arranged one behind the other, so that the perforations in each plate are in staggered relation to those in the next.

(4) By loading the particles with water. Generally this is accomplished by cooling the fume below its dewpoint, so that water vapor condenses upon the particles. The fume may be cooled by passing it through a sheet-iron flue that is exposed to the atmosphere, or by causing it to expand adiabatically in a large settling chamber, where the deposition of moisture upon the suspended particles reinforces the increased settling efficiency that results from the diminished velocity.

(5) By bringing the fume into contact with solid surfaces—for example, strips or sheets of iron suspended in the flue. Dust and smoke particles are deposited upon these surfaces to an extent that is proportional to the area of the surfaces.

There is no doubt that the efficiency of a settling process can be increased greatly by submitting the fume to preliminary flocculation, so that the size of the particles is greatly increased. So far, the mechanism of this process is yet to be worked out, but, in many cases, it would seem that suitable flocculating agents could be added to the fume, and thus reduce the degree of dispersion to such an extent that settling would be greatly accelerated.

Separation by Filtration.

Considerable attention has been directed, particularly in Germany and the United States of America, to the dry filtration of metallurgical smoke. Owing to the enormous volume of smoke to be handled and the low permeability of an effective filtering medium, the filtering area has to be very great. Large fans are necessary to draw or drive the gases through the filters. In most cases, also, the filtering material is an animal or vegetable fiber, and will char or catch fire unless the gases are cooled.

Some of the earliest filters were simply towers filled with dry coke. They soon became choked and were troublesome to clean. They have been superseded by bag filters. The bags are made of wool or cotton, and sometimes asbestos. The smoke is drawn through the walls of the bag, the dust being collected on the surface of the fabric. To remove the dust, the bags are shaken or beaten periodically, or treated with compressed air. The gases must be cooled below 90° C. for cotton, and below 120° C. for wool; otherwise the bags are charred. On the other hand, the temperature of the gases must not fall below the dewpoint of the smoke (50° C.) or the acid will condense on the fabric and rot it.

Bag filtering is really a special form of separation by surface contact. The filter does not behave altogether as a fine sieve, for the interstices of the fabric are much larger than the smoke particles. The particles are first deposited on the fibers, and gradually built up until the bags become choked. Wool is found to be about 50 per cent more efficient than cotton, possibly on account of the scaly surface of its fibers. Also, it is much more durable, although initially it is considerably more expensive. Camel's hair has been used of recent years, and is said to be even better than wool. From 3 to 4 square feet of filtering area are necessary per cubic foot of gas per minute—0.5 square foot, if the bags are cleaned mechanically.

The danger of rotting the fabric with acid gases is sometimes avoided by neutralizing the gases with lime or zinc oxide dust before being filtered. The life of a bag will depend very much upon the kind of dust for which it is used; the sharp dust particles from grinding and buffing shops, for instance, cut the bag and quickly wear it out.

Bag filters are generally less expensive than a washing plant to construct and maintain. They have the additional advantage that they collect the material in a dry state. Their application is limited, however, by the difficulty of obtaining a sufficiently resisting fabric. Also, the power required to draw such large volumes of gases through the bags is very large, particularly when the bags become choked with dust. Asbestos bags and screens are expensive, and become brittle when exposed to hot acid gases. By means of a bag-filtering plant, the dust content of blast furnace gas at 50° C. can be reduced to from 0.01 to 0.001 gram per cubic meter. Bags last from six to twelve months, and the power expended amounts to 1 h.p. per 10,000 cubic feet. For ordinary bag filters, without mechanical cleaning, 1 h.p. is consumed per 3,000 cubic feet of fume.

In some blast furnaces the gases are filtered by passing them through filter mattresses, consisting of metal framework packed with metallic wool. The gas passes in succession through a number of such filters, the texture of the filters becoming progressively finer the more remote they are from the gas inlet. By this means, the dust content of blast furnace gas can be reduced to 0.5 gram per cubic meter. In some cases, dusty gases or smokes are filtered through loose granular materials, such as sand. It has also been proposed to use froths and foams in a similar way.

Separation by Washing.

Many methods have been devised for removing particles from gases by bringing them into contact with water. The aerosol is either driven against a water surface, bubbled through water with violent agitation, drawn or driven through a scrubbing tower against a stream of water, or treated with fine water sprays.

It is difficult to clean a gas efficiently with water. In the first place, it is difficult to make certain that every particle in the gas will come into contact with the water. The intimacy of contact between the aerosol and the water, and, therefore, the efficiency of the washing process, can be improved by increasing the area of the water that is exposed to the gas. The most efficient way of accomplishing this is to pass the aerosol upwards through an absorption tower filled with coke, gravel, slag wool, etc., against a descending stream of water. In this arrangement there is a contest between wetting efficiency and power consumption. If the packing of the tower is coarse enough to allow the gas to pass freely, the particles are not effectively wetted. If the packing is fine enough to bring about intimate contact between the suspended particles and the water, the power consumption is greater, and the spaces between the packing soon become clogged and require frequent cleaning.

Even when complete contact is possible, it does not necessarily follow that the particles will be wetted by the water. Generally speaking, wetting is more easily obtained the lower the interfacial tension is between the particles and the water. Possibly, in some cases, soap solutions would be more effective than water.

Some smoke particles are extremely difficult to wet. The blue zinc oxide smoke from a brass foundry, which is generally diluted with a considerable quantity of air, will pass right through an absorption tower packed with wet coke practically unaffected. This is conceivably due to the presence round each particle of an adsorbed film of gas (air).

The difficulty of wetting smoke particles can be overcome by humidifying the hot gases with water sprays or waste steam to such an extent that, when they are subsequently cooled (for example, by expanding into a large settling chamber, or by passing through a surface condenser), the excess water vapor will condense upon the particles and carry them down with it. In many cases the amount of water vapor originally present in the gas will be sufficient to supersaturate it when it is cooled below 50° C.

Sulphur trioxide mist is difficult to catch with water or weak acid, but can be caught readily with sulphuric acid. The mist is more stable and difficult to catch, the more quickly the SO_3 gas has been cooled. It is probable that each SO_3 particle is protected by an adsorbed gas film. In a mist formed by quick cooling the particles will be smaller, and, therefore, the gas film will be relatively thicker. Apparently, this gas film is readily displaced by H_2SO_4, although not by water.

In addition to the relatively high power consumption required for thorough gas washing, the process is often costly and troublesome in practice, owing to the acid gases in the fume. This necessitates the use of expensive acid-resisting plant.

For certain processes in which the volume of gas is relatively small, washing processes are economically practicable and are well established. They are used successfully with coal gas, producer gas, and for the small proportion of iron blast-furnace gas which is used for gas engines.

Separation by Electrostatic Precipitation.

During the last twenty years the Lodge-Cottrell process of electrostatic precipitation has been applied to a variety of dusty smokes and fumes.

The electrostatic precipitation of smoke is possible with either alternating or direct current. When a smoke is subjected to a high-voltage alternating current discharge the gas is ionized, and the smoke particles become electrically charged by the adsorption of ions from the gas. Owing to the rapidly alternating polarity of the particles, they agglomerate to form large flakes. If the gas is still, or moving very slowly, these flakes will settle. To obtain effective precipitation with an alternating current, it is necessary to have the electrodes very close, and the gas path long, and the gas velocity low.

In practically all industrial problems, however, we have to deal with very large volumes of gas, necessarily travelling at a considerable velocity along flues. In these circumstances it is found that direct current is vastly more effective, since it drives the suspended particles to the surface of the depositing electrode.

When a highly charged wire is fixed opposite to a flat plate at some distance from it, the intervening air space becomes highly charged with electricity of the same sign as the wire, whether it be positive or negative. The intensity of the field between the wire and the plate varies inversely as the distance from the wire. Of the gas ions or charged particles originally present in the air space, some will be attracted by the wire. As they approach the wire their velocity will increase rapidly, owing to the increasing strength of the field, and if the voltage be high enough, their velocity will be so great that they will ionize the intervening gas and the wire itself by the force of their collision with the molecules of the gas and the wire.

In general the wire is negatively charged, so that it is the positively charged ions originally present in the gas that produce this ionization by collision. The negative ions so formed are repelled from the wire, and travel rapidly towards the plate. Any gas molecules or smoke particles present in this intervening space become charged by these ions, and are, therefore, driven by electric force towards the plate. The suspended particles are also driven mechanically by the rush of ions from wire to plate.

This process is described fully elsewhere in this book.

Dust Explosions

When a combustible substance—*e.g.,* sugar, coal, petroleum—is dispersed in air, it will, under certain conditions, burn with explosive violence exactly like a mixture of air and a combustible gas or vapor. An aerosol necessarily has a coarser structure and a higher specific heat than a gas mixture. It will, therefore, ignite less readily and propagate a flame less rapidly than a gas mixture. On the other hand, the quantities of heat and gas that are liberated by the combustion of a unit volume of an aerosol are frequently greater than those that are produced in an explosive gas reaction. It is not surprising, therefore, that dust explosions are frequently as violent and destructive as gas explosions.

The combustion of an aerosol takes place in at least two stages: first, the ignition of the dust at some point, and then the propagation of the flame through the aerosol. Whether the dust particles will ignite depends necessarily upon their nature, and the temperature to which they are raised. When some of the dust becomes ignited it produces heat; this heat, except for that which is lost by radiation, will, by conduction, raise the temperature of the aerosol in its immediate vicinity. In favorable circumstances the temperature of the adjacent gas will be raised to its ignition point, and the dust will ignite. Once initiated, the flame will then spread rapidly through the gas. Where combustion occurs, the gas will expand suddenly and exert a pressure upon the layer of gas adjacent to it that will facilitate ignition. A compression wave will travel through the gas with the velocity of sound. In some cases the magnitude of this compression is sufficient to ignite the mixture. The aerosol will then detonate.

The explosive properties of a large number of dusts have been investigated systematically by Wheeler, Taffanel, Dixon, Price, Beyersdorfer and others. They have traced very clearly and completely the relations that exist between the explosive possibilities of different dusts and their chemical nature and physical condition.

When combustion is initiated at any point, a quantity of heat is liberated at a certain rate. Some of this heat is lost by radiation, but most of it becomes available for heating the adjacent layer of aerosol. Clearly, the maximum heating effect that can be produced will depend upon the quantity of heat that is made available per second, and the specific heat of the adjacent layer of aerosol. Anything which diminishes or retards the production of heat by the burning particles, or which increases the specific heat of the adjacent layer of aerosol, will tend to inhibit the propagation of the flame. The heat produced by different substances varies according to their heat of combustion. Sugar, petroleum, starch, flour, coal, produce far more than oil-cake, wheat offal, leather dust.

For a given substance, the quantity of heat will be greater the lower its content of incombustible matter (ash), and the higher its concentration per unit volume of aerosol, provided that the amount of oxygen present is just sufficient for complete combustion. The heat will be produced more rapidly the higher the degree of dispersion of the dust. If the particles be damp, some of the heat of combustion will be absorbed in evaporating this water, and, therefore, less will be available to warm the adjacent layer of aerosol.

The heat capacity of the aerosol will be increased by the presence of (a) inert gas or dust, (b) an *excess* of the reacting gas or dust, since this excess will necessarily be inactive, (c) water droplets or vapor.

The most reactive conditions are obtained when the substance of the disperse phase is readily inflammable and possesses a high heat of combustion, when the reacting substances are present in their combining proportions, when the aerosol is dry, free from inert impurities and possesses a high degree of dispersion. The practical problem, however, is not to produce dust explosions but to prevent them. The best method of prevention is to prevent the formation of aerosols or of aerogels (that are formed where dust accumulates on walls, rafters and floors). This is generally done either by keeping the work damp, so that the dust cannot "rise," or by drawing it away by suction fans as it is formed—it is then discharged through a shaft or collected in bag filters or other suitable device. Where the formation of the aerosol or aerogel cannot be avoided—for example, in coal mines, and in certain factories and mills—the aerogel can be rendered non-inflammable by diluting it with an inert gas—*e.g.*, flue gases—an inert dust—*e.g.*, slate dust or precipitated chalk—or by keeping the dusty atmosphere moist with water vapor or sprays. None of these precautions would be necessary if all risk of ignition could be eliminated. This has been attempted, but, all too frequently, the dust has been ignited by a broken electric lamp, or a flash from a cut-out switch, or a bearing has seized and become heated above the ignition point of the dust, with disastrous consequences.

In some cases it has been shown that the particles of the disperse phase become electrically charged by friction at the moment of their formation, and that these charges can accumulate sufficiently to produce a spark discharge that is able to ignite the aerosol. This has been shown by Price to be a frequent cause of explosions in threshing machines and in attrition mills. Beyersdorfer has worked out very thoroughly the application of this theory to the explosion of sugar dust. Incidentally, he has suggested that the destruction of Sodom and Gomorrah by a rain "of brimstone and fire" can be attributed to a charged mist of petroleum formed in the Caucasus by the outburst of an oil spring, and carried southwards to the cities of the plain. There it reached the isoelectric point, flocculated, and was precipitated as rain and became ignited by lightning. Similar self-ignited oil-clouds are a familiar phenomenon in the Caucasus.

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Atmospheric Nucleation

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1. Mr. John Aitken,[1] who pioneered the meteorology of "dust" as he called it, to a point of formidable importance, described two forms of apparatus for measuring the dust content of atmospheric air. One is the well known dust counter, in which the number of particles precipitated on a plate from a definite volume of samples of moistened air, by sudden expansion, are directly counted under a lens. It has been widely used, is portable, catches all particles from Aitken's point of view, and its trustworthiness is assured by the consistency of the results obtained by means of it. The other, called the Koniscope, takes advantage of the axial colors of cloudy condensation. Its scope is limited, the color scale vague and not easily understood. It is with the first apparatus that Aitken furnished the original proof that nuclei are necessary for condensation even in supersaturated vapor and that Aitken and others conducted their varied experiments of the nucleation on mountain and in valley, which it is not necessary to discuss here.

2. These decisive experimental results are in complete conformity with the famous paper of Lord Kelvin,[2] published as long ago as 1870, in which the vapor pressure at any curved surface is fully determined (vapor pressure excess, $\Delta\rho = 2\rho_v T/\rho_e R$, where ρ_v, ρ_e are the densities of vapor and liquid, T the surface tension and R the radius of the drop). It seemed therefore that the subject might be regarded as finished from a theoretical viewpoint and that statistical information only was henceforth to be expected. Nevertheless the failure of Assmann [3] (1885) in a microscopic search (up to 3×10^{-5} cm.) for the nuclei of evaporated drops, the absence of a nucleation increment adequately equivalent to the triturated dust content of air (Wigand, 1912), the fact that the distance of distinct visibility for a given nucleation varied inversely as the dampness of the air (Wegener, 1910) and similar data which gradually accumulated—all these indicated that the presence of mere dust does not adequately account for the observed phenomena. The powerful nucleators are bodies which produce highly dispersed, hygroscopic or at least soluble, products. This is the case preëminently with the emanations of phosphorus,[4] and with the sulphur flame (SO_2) or even with hot melted sulphur. An ordinary flame, apart from its own contributions, volatilizes the salt and other floating particles entrapped. The salt content of glowing charcoal probably operates similarly. The ions which are frequently produced in association with nuclei are without bearing on the present question, since only very small supersaturations are here employed, in contrast to the fourfold supersaturation needed to condense water vapor even on negative ions. Phosphorus emanation in the lapse of time will produce a blue fog spontaneously in merely saturated air. The recent analyses by Köhler [5] of the uncontaminated or frozen closed particles caught on the mountains in northern Norway shows them to be rich in chlorides, even calcium chloride being present.

These converging lines of evidence, therefore, imply that the meteorologically important nucleus is the solutional water nucleus; *i.e.*, a nucleus in which the vapor pressure increment resulting from curvature is counterbalanced by the vapor pressure decrement due to solution ($\Delta p/p = (m/M)(\mu/\mu')$, where Δp is the decrement in question, m/M the concentration of the solution, and μ/μ' the ratio of molecular weights of solvent and solute). Such a nucleus will not vanish. It may grow by virtue of its salt content until the surface vapor pressure, determined by curvature alone, is below the supersaturation of the surrounding air and thereafter grow indefinitely. It is exceedingly curious to find that even when a fog is artificially precipitated on ions and again evaporated, the ions are thereafter represented by water nuclei upon which precipitation may be made almost without supersaturation. The theoretical treatment of the condensation on ions is given at length by Sir J. J. Thomson,[6] who shows that in case of electric charge e, the term $2T/R$ is to be replaced by $2T/R - e^2/8\pi KR^4$, where K is the specific inductive capacity of the medium. In a saturated atmosphere the drop will therefore grow until the R makes the binomial zero. Similarly, a brush discharge either from metal terminals or from glass, nucleates powerfully. Nuclei produced when two opposed filamentary jets of tap water mutually impinge on each other disruptively, endwise, are quite persistent in a saturated region. Their electrical charge vanishes at once, but the nuclei may be used for the precipitation of cloud particles in the fog chamber indefinitely.

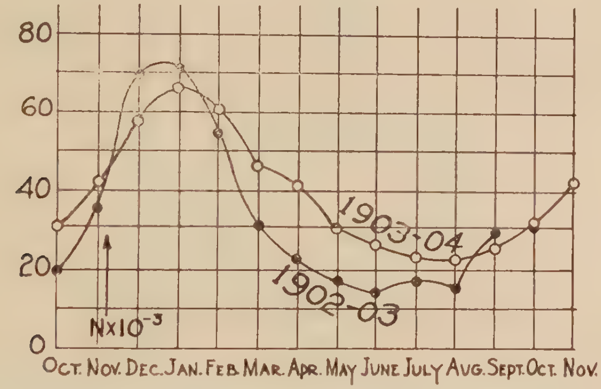

Fig. 1.

Between the years 1902 and 1905 a systematic study of the nucleation of the atmosphere was undertaken at Brown University in the city of Providence and as the results bear directly on the subject at issue, they may be briefly quoted. Since the observations were to be made at a fixed station, a capacious fog chamber was chosen, through which the air continually circulated. The diameter of fog particles and hence their mass m for a given adiabatic expansion within the chamber may be obtained optically from the aperture of the coronas of cloudy condensation. These coronas are in almost all cases white centered and red ringed, or normal, so that the usual equations for the diffraction of light by a single particle are available.

The quantity of moisture (M) precipitated per cubic cm. by the definite expansion in question may be deduced from an entropy temperature diagram for water vapor.[7] The two quantities together give us the number of nuclei $(Nm = M)$ per cubic cm. required. It is thus merely necessary to make an exhaustion and measure the diameters of corona produced by a simple goniometer, to obtain N and the method is accurate enough for the purposes.

Observations of this kind were taken several times a day, averaged for the day and subsequently for the month. The results for the year 1902-03 and 1903-04 are summarized in the diagram, Fig. 1, the nucleation N being laid off vertically in thousands per cubic cm. It is seen at once that the winter nucleation is enormously in excess over the summer nucleation. The monthly average may be larger than $N = 70{,}000$. The mean daily data often exceed 100,000. It is a startling contrast that on an exceptionally cold, very clear winter's day, when everything is frozen fast, one obtains these enormous nucleations, whereas on a windy dusty dry summer day, the nucleation may be relatively negligible. The lowest values occur during rainy days and N may then fall to a few thousand.

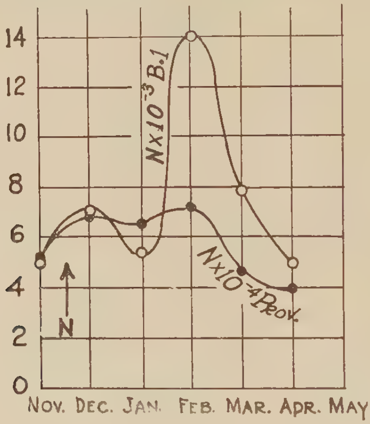

Fig. 2.

In Fig. 2, the nucleation surrounding Brown University in 1904-05 in *ten thousands* per cubic cm. is compared with the contemporaneous nucleation in *thousands* per cubic cm., found by Mr. Robinson Pierce, at Block Island. Block Island is in the ocean at a minimum distance of about 20 kilom. from the mainland and about 70 kilom. from Providence. Nevertheless the two nucleations in their maxima and minima are the same in character at both places. The Providence nucleations are 5 to 10 times larger, but the underlying source is the same. The 1904-05 graphs, moreover, have a peculiar development in February due to meteorological occurrences not present in the earlier graphs.

Apart from details, mere inspection of the curves shows that the active nuclei here are products of combustion and that the highly dispersed soluble materials are wafted some distance out above into the ocean.

As a whole the phenomena of atmospheric nucleation are based on a rather clearcut and relatively simple principle. The term *colloidal* referred to them, as was done in much of my work,[8] seems superfluous. True, the nucleation obtained by a brush discharge in air would in a liquid produce a colloidal metallic or other solution; but the dispersion in air ceases to present other than easily interpretable solutional and capillary phenomena.

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Colloid Meteorology

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There are good people who contemptuously scorn pork until someone kindly calls it veal, whereupon they devour it ravenously. Perhaps a similar concession to the colloidist in respect to meteorology may also produce a happy result. At any rate this concession is easy to make, for liquid or solid particles, larger than single molecules, floating in the air constitute, with this air itself, an *aerosol,* and an *aerosol* is, by definition, *a* colloid. Colloid meteorology, then, treats of those phenomena that are owing to the presence of minute foreign bodies in the atmosphere, that is, of condensation in the free air, and of certain optical and electric effects.

Nature and Origin.

Excluding, for the present, fog and cloud particles, to be discussed separately, there still are many kinds of colloidons (particles of colloid size of whatever state, shape, and composition) in the atmosphere, and their sources are numerous. Among these kinds are: 1. Mineral dust, finely pulverized or disintegrated rock with or without chemical change, caught up by surface winds. 2. Vegetable fibers, largely caught up by the wind from soil. 3. Pollen, especially from conifers and other heavy pollen-bearing trees. 4. Soot, unburnt carbon particles and mineral ash given out from fires of every type. 5. Salt particles resulting from the evaporation of ocean spray. 6. Hygroscopic droplets, formed by the solutional union of water vapor with such hygroscopic gases as ammonia and the oxides of nitrogen, produced by electric discharges, and the oxides of sulphur, SO_2 chiefly from the burning of coal, and SO_3 apparently from the action of ultraviolet radiation on SO_2. 7. Volcanic "ash" explosively ejected and, in some cases, wind blown to the ends of the earth. 8. Meteoric or cosmical dust, the ashes, so to speak, of incinerated meteors, or shooting stars, of which, on the average, millions flash through our atmosphere every day. 9. Spores, microbes, bacteria, et cetera, scattered through the air by winds and convection currents.

These, of course, are by no means all the kinds and sources of colloidons, but they appear to be the chief ones, and, at any rate, are sufficient to persuade us that what we breathe is not pure air but a highly complex aerosol of at least 10^{22} gas molecules and a million micro-sticks and -stones for every average breath.

Distribution.

Again excluding fogs and clouds, the konisphere (dust sphere) is coincident with the atmosphere, and, like the latter, divisible into more or less distinct layers. These are:

1. The turbulence layer, next to the surface and of varying depth up to a kilometer, roughly, but generally much less. It is the region of mechanical, or surface, turbulence of the air, which agitation fills the space involved with larger colloidons and a greater number per unit volume than are in any other portion of the whole konisphere. This layer often is seen from mountains as a haze, with a more or less sharply defined upper surface—the top of the turbulent air.

2. The convection layer, resulting from the carrying up of the relatively dusty surface air by thermal convection. It is deepest and dustiest therefore during summer droughts. Its upper surface, often three kilometers, roughly, above the earth, frequently is a sharply horizoned ocean, as viewed from an aeroplane, in which cumulus clouds stand like islands in the sea.

3. The tropic layer, coincident with the troposphere, or all that portion of the atmosphere from the surface of the earth up to the limit of vertical convection, or, therefore, to the tops of the highest clouds. In middle latitudes, the depth of this layer is 10 to 12 kilometers. In high latitudes its depth is less, and in equatorial regions decidedly greater. Its surface seldom is seen, owing to its great height, but that a dust layer boundary occurs at this level is evident from certain polarization phenomena of skylight. It also is evident from the fact that vertical convection of the lower air, laden with terrestrial dust, does at times reach this limit, but never goes beyond it—this being the level below which temperature rapidly changes, and above which it remains substantially constant, with change of height.

4. The stratic layer, coincident with the stratosphere, or all the atmosphere beyond the troposphere. The colloidons of this region come from the daily millions of meteors, and the occasional violent volcanic explosions of the Krakatoa and Katmai type. Presumably there also are present, owing to insolation and electric discharges, hygroscopic molecules, especially nitrogen peroxide, which help to keep up the supply of condensation nuclei at the upper level of cirrus clouds.

The tropic and stratic dust layers are always present, but the amount of dust in each varies greatly. The dustiness of the stratic layer is varied mainly through volcanic explosions. At times, such for instance as the year or two following the outbreak of Krakatoa, this dustiness is so great as seriously to affect the intensity of sunshine as received at the surface of the earth.* However, after a greater or less interval, generally one to four or five years, this dust settles out and the stratic layer contains only the particles or colloidons of cosmic origin, and those, if they occur, of insolational origin.

All three of the lower dust layers, those pertaining to the troposphere, are subject to frequent and rapid changes in the amount of their dust content. General rains and snows leave the atmosphere in which the condensation occurs and through which the precipitate falls comparatively dust-free. On the other hand, the winds and convection of dry hot weather carry up dust again in abundance. Obviously, too, the average size and mass of the individual particles decrease with increase of height, both from layer to layer and within each individual layer.

Condensation.

The amount of water vapor necessary to produce saturation (state of equilibrium of vapor pressure in the presence of a flat surface of pure water) increases rapidly with increase of temperature. Hence by cooling saturated air one can easily determine the effects, under different conditions, of supersaturation. Whenever, for instance, ordinary air, kept saturated by the presence of water, is suddenly expanded, as easily managed in a suitable closed vessel, the consequent dynamical decrease of temperature produces a corresponding supersaturation resulting in the production of a miniature fog or cloud. After these minute droplets have settled, which they do slowly, a second sudden cooling produces another, but much thinner, cloud. Subsequent moderate coolings, however, after the first few, fail to produce any cloud particles. Similar effects follow the admission of momentary spurts of live steam into the closed vessel—another way of producing supersaturation. If filtered air, that is, air that is drawn through several inches of cotton wool, or other substance of similar texture, is used, condensation by moderate cooling is impossible from the first. The admission of a puff of smoke, however, restores to the exhausted air, and endows the filtered air with, full powers of condensation.

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* In ancient times, the eruption of volcanos may have been a material factor in affecting climate. J. A.

Clearly, then, there are in tobacco smoke,* for instance, and in ordinary air, condensation nuclei, usually hundreds and often thousands per cubic centimeter, upon which water gathers as soon as saturation is closely attained, or, at most, slightly passed. The great majority at least of these nuclei are colloidons. Some may be too big to justify that title. They are not all equally effective, however, as condensation nuclei, owing to the varying degrees to which the several kinds are hygroscopic. Granules of sea-salt for instance. the principal ocean dust, are much more hygroscopic than most kinds of land dust. That is, at the same temperature, the equilibrium vapor pressure over damp salt is less than that over many damp soil materials, such as quartz sand.

Obviously, therefore, when the percentage of saturation is continuously increased in a body of air that contains, as does the free atmosphere, several kinds of dust, or nuclei, quite differently hygroscopic, condensation occurs first on that kind in which this property is most pronounced.† As the first droplets grow their vapor tension increases, owing to dilution, until presently condensation extends to the next most hygroscopic nuclei, and so on, as long as any nuclei are present. Hence, so long as there is present an abundance of quite hygroscopic nuclei, the addition of relatively non-hygroscopic dust does not alter the number of fog or cloud particles per unit volume, nor, therefore, the density or opacity of the fog or cloud. The actual condensation nuclei, then, that is, those on which condensation really occurs, are only the more hygroscopic colloidons present, whatever they may be. Every floating mote, however, is a potential condensation nucleus, a reserve as it were, that immediately comes into action as soon as the more hygroscopic ones have either been rendered enough less efficient by dilution or dragged quite out of the field by their accumulated aqueous loads.

In "dust" free but ionized air condensation begins on the negative ions when the humidity has attained about a fourfold supersaturation, and on the positive ions at about the sixfold stage. If neither dust nor ions are present, condensation still may be forced, but only by at least an eightfold supersaturation. There is no reason, however, to believe that any such degrees of supersaturation occur in natural meteorological processes. Furthermore, the ions and the neutral molecules that, in these cases, are the nuclei of condensation are too small to be admitted to the family of colloidons. Of course, though, the droplets thus formed pass through every gradation of the colloidon size. Nevertheless, they have no meteorological interest, being formed only under highly artificial laboratory conditions.

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* Zsigmondy and others have examined tobacco ultramicroscopically. J. A.

† See H. A. Wilson's Cloud method in Millikan's paper, p. 174. J. A.

Equilibrium Vapor Tension of Droplets.

As stated above, the vapor tension of a droplet depends on the quantity and kind of substance dissolved in it. In any case it is greater than that of a flat surface of the same solution, and to an extent that varies inversely with the radius of the droplet, as shown first by Sir William Thomson[1] long ago.

To find an expression for this difference of vapor tension at the same temperature, let a capillary tube of circular cross section stand vertically in a dish of water enclosed by a bell jar or other vessel, so as to secure saturation, from which all air has been exhausted. Let the height, h, of the water in the tube above its level outside be many times the inner radius R, so that the meniscus shall be very nearly spherical, and let the angle of contact between water and tube wall be 0°, as it is, at least very closely, when the tube is glass. Let T be the surface tension, and ρ_w the density of the water, ρ_v the average density through h of the saturated vapor, g the gravity acceleration, and Δp the difference between the vapor pressures at the inner and outer surfaces.* Then, since the pull up on the capillary column by the surface tension is equal to the total pull down

$$2\pi RT = \pi R^2(\rho_w - \rho_v)gh \tag{1}$$

But

$$\Delta p = \rho_v gh$$

Hence, substituting in this second equation the value of gh from equation (1),

$$\Delta p = \frac{2T\rho_v}{R(\rho_w - \rho_v)}, \tag{2}$$

negative for concave surfaces, and positive for all that are convex.

For a droplet whose diameter is 10^{-4} cm., this increase of vapor tension is, at ordinary temperatures, approximately that which would be produced over a flat water surface by an increase of temperature of about .02° C. The increase of equilibrium by fog and cloud particles, average diameters about 10 μ and 33 μ, respectively, is in each case much less than that cited, they being larger droplets; nevertheless it is of importance.

If other things were equal, the smaller droplets, having, for the reason just explained, the greater vapor tension, would shrink by evaporation and the larger grow by condensation. But other things are not equal. Many of the condensation nuclei are soluble; hence the vapor tension of a droplet formed about such a nucleus tends to become less with decrease of size owing to increase of concentration, and greater owing to increase of curvature. These opposing effects speedily produce a balance under which all droplets about soluble and hygroscopic particles have roughly the same size, while the comparatively non-hygroscopic colloidons remain inactive.

Equation (2), that gives the relation of surface curvature to equilibrium vapor pressure, shows that condensation must be more and more difficult as the size of the nucleus becomes less and less, and impossible, it would seem, without nuclei of some kind. But experiment shows that condensation does take place in the absence of all nuclei as soon as the vapor has attained an approximately eightfold supersaturation. Clearly, then, equation (2) does not hold indefinitely with decrease of size of droplet, probably because when it is less than a certain very small size the surface forces at every point on the droplet are disturbed by those of every other point, though the details of how this comes about are not known.*

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* The R and T here must not be confused with the gas constant R and the absolute temperature T. J. A.

It also is clear from equation (2) that condensation must occur first and most freely in the interstices, and on the concave portions of nuclei, and that the droplets must therefore be spherical from very near the beginning of their formation.

Coronas.

Coronas consist of one or more concentric rings of colored light, or systems of such rings, about a luminous center, such as the sun or moon. They are produced by the diffraction of light from a distant source by a sheet-like distribution of small spherical, or roundish, particles of approximately the same size.

It is known from experiment that light is transmitted from one place to another as though by waves, or at least by a process that possesses certain wave properties. We even speak of the wave front of light, meaning a continuous sheet at every point of which the wave phase, or what behaves like a wave phase, is the same. Hence, to find the effect at a specified place of a given portion of such a wave front we have only to regard each infinitesimal area over this portion of the wave front as a center from which the energy of that area radiates equally in all directions, and to integrate, for the point in question, over the given portion of the wave front. A simple way of solving such a problem experimentally is to pass monochromatic light through a small opening, circle, slit, or what not, in an opaque screen, and note the illumination of a suitable surface beyond the opening. If the incident light is parallel and passed through a narrow rectangular opening, a series of bright and dark lines parallel to the slit will appear on the receiving screen, symmetrical on either side of the projection of the slit, and progressively finer and closer together with increase of distance from the center of that projection. A small circular opening produces concentric rings of light, finer and closer together with increase of their radii. Every small opening, whatever its shape, produces its own set of fringes, all outside the geometrical projection of the opening onto the receiving screen. These light effects outside the geometrical projection of the opening and within the "shadow" of the opaque screen are diffraction phenomena, and the action that bends, as it were, the light out of its straight line course is *diffraction*. Clearly, then, a thin cloud sheet, for example, of water droplets may be regarded as the equivalent of so many opaque circular disks evenly scattered over a transparent screen. In this case the transparent portions of the screen, or effective parts of the wave front, would be of irregular shapes, impracticable to integrate over for their combined effect at any given point. However, the diffraction effect of opaque disks of uniform size scattered over a transparent screen is precisely the same as that of an equal number of circular holes of equal size similarly distributed over an opaque screen. This furnishes a mathematically manageable problem, and its solution is the solution of the corona, so often seen, when the clouds are very thin, about the sun and the moon. A similarly formed corona, known as Bishop's Ring, 15° to 20° radius, occasionally is seen about the sun after violent volcanic explosions of the Krakatoa and Katmai type. This ring is owing to the diffraction of the sunlight by the very fine dust in the upper atmosphere beyond the reach of the highest clouds.

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* Regarding this, see paper by I. Langmuir, this volume. J. A.

The above outline of what diffraction is, and hint as to how the problems it presents may be solved, are sufficient for a general understanding of the subject. The more or less tedious mathematics necessary in the quantitative solutions of such problems may be found in various works on optics. The problem of the corona and other meteorological diffraction phenomena is solved in detail in such generally available and recent books as Pernter and Exner's "Meteorologische Optik," and Humphreys, "Physics of the Air."

The most significant corona equation, perhaps, in its relation to colloids, derived in the treatises referred to, is

$$\sin \theta = (n + 0.22) \frac{\lambda}{2a}$$

very nearly, in which θ is the angular radius of the nth ring of minimum brightness of a corona, counting from the center, λ the wave length of the incident light, and a the common radius (all the same) of the diffracting droplets.

By measuring θ, easily done with a theodolite or other suitable instrument, corresponding to $n = 1$, $n = 2$, or other small whole number, for any selected color, or approximately definite value of λ, one obtains by the simplest arithmetic the diameter, $2a$, of the particle in question.

In this way it has been found that the diameters of liquid cloud droplets commonly range from .014 mm. to .040 mm., clustering about .033 mm.; that the average diameter of fog droplets is, roughly, .010 mm.; and that the width, or diameter of the long suspended Krakatoa dust particle was approximately .00182 mm. (1.82 μ).

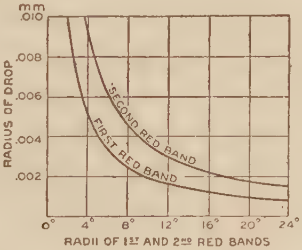

Fig. 1.—Relation between size of drop and size of corona (after Simpson).

Iridescent Cloud.

There is another meteorological phenomenon, of rare beauty, that belongs to the corona family, viz., the iridescent cloud. The best forms of this, often of considerable extent, occur 15° to 30° from the sun in thin high clouds of the alto-cumulus and alto-stratus types, and consist of irregular and intermingled splotches of pearly pinks and delicate greens. These patches of exquisite color, and hence the whole iridescent phenomenon, are only portions of a very large corona formed, therefore, by exceptionally small droplets.

The relation between the linear radius of droplets and the angular radius of the corona, including iridescent clouds, they produce, is shown in Fig. 1.

Rainbow.

Some authors regard the rainbow, and especially the pale, broad fogbow, as a colloid phenomenon. However, the raindrop, at least, by which the bow is best formed, certainly is extra-colloidal in size. The tedious (if adequate) discussion of this phenomenon therefore will be omitted. Those who wish to know the theory of, and principal facts concerning, this meteor can find them in considerable detail in the works on Meteorological Optics and Physics of the Air referred to above.

Halo.

There are many well known halos—rings, splotches and arcs, both white and tinted, symmetrically placed about the sun or moon. These, too, some authors would class as colloid phenomena. But they are formed by ice columns and tablets, of appreciable size, say half a millimeter to a millimeter long, if columnar, or broad, if tabular. It would seem allowable therefore to exclude such hunks of ice from the family of tiny colloidons, and with them all the delicate, symmetrical, and beautiful halos they hang in the sky. The story of the halo, long and interesting, may be found most readily perhaps in the same books referred to under the Rainbow.

Sky Colors.

Not until modern times did anyone go on record, so far as we know, as asking why the sky is blue. The first answer was the one so familiar to children, and, to the brighter ones, so unsatisfactory, namely, "That is its nature." Of course, the wise men that gave this illuminating answer soon were asked "How does it get that nature?" Various attempts were made to answer this question, but without avail, until 1871, when the late Lord Rayleigh[2] formulated a theory so full and complete as to account for every known fact of observation and experiment.

It is unnecessary to repeat here the substance of Rayleigh's searching analysis of this problem. His original papers are easily available, as are also many summaries of them in works on optics, and also in the two meteorological works above referred to. Some of Rayleigh's most important conclusions, in regard to the action of molecules and colloidons on light, are embodied in the following equation, based on the assumption that the scattering particles are identical, equally numerous throughout the scattering layer, not too close together, and small in comparison with the cube of the wave length of light used:

$$I_1 = I_0 \frac{4\pi^2(\mu - 1)^2 \sin^2 \alpha}{n^2 r^2 \lambda^4} e^{-\frac{32\pi^3(\mu - 1)^2)x}{3n\lambda^4}}, \text{ nearly}$$

$$\equiv I_0 \frac{k}{\lambda^4} e^{-\frac{cx}{\lambda^4}} \tag{3}$$

in which

I_0 = initial intensity of incident light;
λ = the wave length of the incident light;
n = the number of scattering particles, all alike, per unit volume;
I_1 = intensity of light received from a single scattering particle;

x = length of path of incident light through layer to particle giving the light in question;
r = distance from the given particle to observer;
α = the angle between paths of incident and scattered lights;
μ = refractive index of medium, air, say, or other substance, whose index is quite small.
$e = 2.71828 \ldots\ldots$, the base of natural or Naperian logarithms.

This equation embodies the fact that the intensity of the light scattered by a minute particle (similarly of course for many particles) varies directly as the intensity of the light incident on that particle, as the square of the sine of the angle of deviation from the path of incidence, and as the square of the refractivity, $(\mu - 1)$, of the medium; and inversely as the square of the packing (number of particles per unit volume), square of the distance from the place of scattering, and the fourth power of the wave length.

Clearly, from the exponential or extinction term of this equation, light of very short wave length is rapidly enfeebled as it penetrates the scattering layer. Similarly, from the scatter term, very little light of long wave length is diffused by the minute particles. The dominating color of sky light therefore should lie somewhere between that of the most scattered radiation and that of the least scattered, that is, between that of the shortest wave length and that of the longest wave length, and so, in general it does. Ordinarily, as all know, the color of the sky is neither violet nor red, but blue, a color of intermediate wave length.

Equation (3) shows, among other things, that the dominating color received at the surface of the earth, or any other given level, from a given quantity of scattering particles depends on the height of these particles.

As before, let the packing of the diffusing or scattering particles be the same, then solving (3) for dominant color, that is, for the maximum value of the ratio of I_1/I_0, we get, where m signifies maximum

$$\lambda^4{}_m = cx. \tag{4}$$

Hence, in general,

$$I_1/I_0 = \left(\frac{I_1}{I_0}\right)_m \left(\frac{\lambda_m}{\lambda}\right)^4 e^{\,1-\left(\frac{\lambda_m}{\lambda}\right)^4}$$

From Equation (4) it appears that the wave length of the dominating color increases with the distance x of penetration of the incident light through the scattering layer. This explains in large measure why the twilight sky runs the spectrum gamut from blue to red in the evening, and red to blue in the morning.

In the case of direct light the ratio of initial to residual intensity is given by the equation

$$I_1/I_0 = e^{-\frac{cx}{\lambda^4}},$$

as may be inferred from (3), this being the term that does not involve the distance r. But c in this expression is proportional to the square of the volume of the scattering particle, a value implicitly contained in the square of the refractivity, $\mu - 1$. Hence the larger the scattering particle, other things being the same, the feebler the residual light of any given wave length. Furthermore, since the extinction coefficient, c/λ^4, varies inversely as the fourth power of the wave length, it follows that with increase in size of the particles the residual direct light becomes more and more prevailingly that of the longer wave lengths.

This explains why, with increasing humidity, and consequent growth in size of hygroscopic particles in the atmosphere, the sun and moon become more and more reddish hued. It explains too the scientific basis of the old saying:

"A red sun has water in his eye."

—a well known indication of an approaching rain. However, the same general effect may, and often does, occur in dry weather owing to smoke from forest fires or other extensive conflagrations.

Haze Cutting.

From the foregoing it is evident that on sunshiny days a distant object necessarily is more or less dimly seen, owing both to the enfeebling by scattering of the direct light from the object itself and to the glare of sunlight scattered by the intervening particles along the line of sight. Hence a passing cloud, shading the intervening region between object and observer, often enables one to see such object far more distinctly, merely, of course, by cutting out the glare. Furthermore, since the scattering is inversely proportional to the fourth power of the wave length of the incident light, a filter, such as yellow or red glass, through which the light of shorter wave length cannot pass, frequently makes the seeing much better, also merely by excluding much of the glare. Such an instrument has been given the descriptive name "haze cutter" since it greatly improves both visual and photographic clearness and definition.

Sky Polarization.

Ordinary sunlight, as also artificial light, will pass through any transparent substance no matter how that substance is oriented with reference to the beam of light. If, however, the transparent object happens to be a slab of tourmaline cut parallel to the long axis of the crystal the light that gets through will pass also through a second slab of tourmaline parallel, with respect to crystal structure, to the first, but will not pass through the second slab if crystallographically it is set at right angles to the first. The light then that has passed through a slab of tourmaline is different from ordinary light, being one-sided as it were, and we designate it as *polarized*. Now, polarized light may be obtained in various ways, one of which is by scattering ordinary, or non-polarized, light by excessively fine particles such as molecules and colloidons. Skylight, therefore, is partially polarized, the proportion of polarization by the first scattering, as computed by Rayleigh,[3] being given by the equation

$$\frac{\text{polarized light}}{\text{total light}} = \frac{\sin^2 \gamma}{1 + \cos^2 \gamma}$$

where γ is the angle between the directions to the sun and point of the sky observed.

At 90° from the sun, then, the once, or primarily, scattered light should be completely polarized. But by actual observation the polarization along this circle, while very great, is not complete. There are at least two important reasons for this. The scattering particles are not all minute in comparison with the cube of the wave length of the scattered light, and, especially, the scattered light is itself scattered a second time, this in turn a third time, and so on indefinitely. Each of these adds its own contribution to the resultant, though, indeed, after the second scattering the quantities are too small to increase perceptibly the light observed.

The details, requiring mathematical analysis, of how the secondary scattering affects the net polarization of skylight may be found in the papers and books already referred to. The principal facts, indicated by theory and found by observation are as follows, copied from "Physics of the Air":

1. Part of the light from nearly all points in a clear sky is plane polarized, whatever the season, location, altitude of the sun, or other conditions.
2. The polarized portion of sky light, in turn, is divisible into two parts: (a) the positive, due to the first or primary scattering, in which the plane of polarization (plane normal to the vibrations) is given by the source (sun), point of observation, and eye of the observer; and (b) the negative, due to secondary scattering, in which the plane of polarization is normal to that of the primary, and, therefore, because of the ring-like distribution of the atmosphere about any point on the earth's surface, essentially horizontal.
3. Generally speaking, the percentage of polarized light along any great circle connecting the sun and the antisolar point increases from zero near either to a maximum midway between them, which, in turn, increases with the altitude of the point in question.
4. The point of absolute maximum polarization is in the solar vertical and ordinarily about 90°, as stated, from the sun.
5. In general, the percentage of polarization decreases with the amount of light reflected through the sky, whether from the surface or from relatively large particles in suspension. It therefore decreases with (a) percentage of snow covering; (b) percentage of cloudiness; (c) dustiness, or anything that itself leads to an increase of dustiness, such as high winds, especially over arid regions, but everywhere during dry weather, strong vertical convection—hence, generally less during summer than winter—volcanic explosions of the Krakatoa type, etc.
6. The percentage of polarization generally increases with the wave length of the light examined.
7. Even shaded masses of air, if exposed to sky radiation, emit perceptible amounts of polarized light.
8. Three small regions of unpolarized light, Babinet's, Brewster's and Arago's neutral points, occur on the solar vertical; the first some 15° to 20° above the sun, the second about the same distance below it, and the third 20° roughly above the antisolar point.
9. As the sun rises above or sinks below the horizon the antisolar distance of Arago's point increases from about 20° to, roughly 23°; while the solar distance of Babinet's point decreases from a maximum of, approximately, 20° to, perhaps, 18°, for a solar depression of 5° or 6°, and to 0°, as does also Brewster's point, as the zenith is approached.
10. When the upper atmosphere is greatly turbid, as it has often been after violent volcanic explosions, other neutral points, in addition to those above mentioned, are occasionally observed.

Electrical Effects.

The foreign particles in the atmosphere, whether fog and cloud droplets, or colloidons of whatever kind, are traps both for the electron and for the positive atomic ion. They constitute the slow moving or Langevin ions—slow moving owing to their relatively great size. This loading of the ions correspondingly decreases their velocity, that is, and to that extent, decreases the electrical conductivity of the atmosphere.

Many other atmospheric phenomena might, of course, by analogy or otherwise, be classed as colloidal, but such a classification and treatment would, it is believed, be largely forced and artificial. It is suggested, therefore, that those who wish any such additional information go to the more customary sources for it. Some flesh indeed is veal, but this banquet name of the fatted calf does not properly belong to all meat!

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Many atmospheric phenomena, in common with phenomena in most other fields, involve colloidal dispersions and the same principles which govern their behavior. If there be any prodigal sons of science who have followed their own specialties so closely as to lose contact with the wide-spreading shrine of science, perhaps they will welcome the fatted calf under the name of veal, even if they erroneously believe it to be pork. J. A.

Colloidal Forms of Water and Ice *

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Atmospheric conditions have been studied and the sizes of fog and mist particles have been estimated with a generally accepted explanation of the precipitation of the water vapor on certain minute particles or nuclei which have formed a center for starting the condensation. The work of Carl Barus[2] has shown us what is probably the explanation of these nuclei, but it does not appear at all clear how the copious and often repeated nucleation in a foggy atmosphere, particularly in winter, can be entirely accounted for by the presence in the atmosphere of finely divided matter in the form of dust.

It is probable that the nuclei are supplied from the water vapor particles themselves which under the action of daylight are made to coalesce from the molecular state to large aggregates of colloidal dimensions.

It is not always realized that the flooding of the atmosphere by daylight results in the projection into the sea of molecules of high powered energy impulses which tear their way through, upsetting the stability and interfering with the molecular equilibrium.†

From the extent of the sun's spectrum, there are always present wave lengths of energy which will suit a wide variety of particles.

The resonant effects in the varying sizes of atmospheric aggregates are responsible for the beauty of the sunrise and sunset. Colorful effects due to selective resonant qualities of any medium are too well known to require extended discussion here. From the easily demonstrated colloidal solutions we can pass to the more delicate coloring of water and ice which will now occupy our attention at the outset of this paper.

The Color of Water and Ice

It appears to be now a matter of general knowledge that water is a highly associated liquid. Evidence is at hand from all the physical properties of water to show that this is so.

There exist in solution molecular aggregates which possess the same physical characteristics as ice. These particles influence the shape of the temperature variation curves of density, specific heat and viscosity, as I showed, many years ago, from a study of the variation of the specific heat of water with temperature. Water contains dissolved ice molecules, and the concentration of this solution increases with falling temperature down to the freezing point, where saturation causes the solid ice to separate out. (Röntgen, 1892.)

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* This paper was prepared at the request of Mr. Jerome Alexander, colloid chemist of New York City, but it was with some diffidence that I consented to correlate some of the many natural phenomena which are produced by finely divided water and ice particles.[1]

† See papers by C. Barus and by R. Audubert, this volume. J. A.

There have been a great many papers written on the association of water,[1a] and many attempts made to find the molecular complex of the ice molecule, which has resulted in the general agreement that ice is to be reckoned as trihydrol, water as dihydrol, and vapor as hydrol, meaning by hydrol the molecule simplex H_2O. Bragg has worked out the crystal structure of ice from theory, and the picture he gives is of surprising interest. The actual experimental results by X-ray analysis, however, do not accord accurately with the theory and do not even agree together. We do not know how the ice crystal is modified by its manner and temperature of formation and until we do we cannot expect better agreement.* The manner of producing the ice is of fundamental importance for the X-ray study.

The beginning of the true colloidal form in water is from the dihydrol which merges into the trihydrol at temperatures below 60° C. to the final ice molecule devoid of all crystal form, where it remains still invisible until the freezing point is reached. At this temperature it becomes sufficiently concentrated, and of sufficient size with relation to the remaining dihydrol molecules, to affect the rays of light which are reflected from the depths of the water, producing a change of hue indescribably delicate and illusive. Old river men are enabled to tell without instruments when the water arrives at the freezing point prior to the early anticipated and much dreaded production of the first finely divided and exceedingly transparent frazil ice. In passing through this change there is evidence to show that the primitive crystal form of the ice is triangular, supporting the theory of the three groups in the trihydrol. The eventual form of the ice crystal is hexagonal, but Bragg proves this to be a complex structure consisting of interpenetrating trigonal prisms. The trigonal form may even persist to modify the hexagonal crystal and many good sized three-sided ice crystal shapes have been recognized.

Iceberg Ice

The color of iceberg ice, which is so vivid in its beautiful blue tone, is probably due to the influence of large group molecules, connected with the presence of the ice molecules in water. Prof. Raman of Calcutta in his address before the British Association in Toronto last summer (1924) tried to prove that the color of water and ice was due to molecular scattering. It was pointed out in criticism that the Tyndall effect in ice or water was due to dust and that it is impossible to get either entirely free from it. In the case of ice this criticism falls down, for the color of ice is a good indication of its manner of formation, and to anyone used to comparing samples, it is easy to distinguish between samples produced under conditions prohibiting the presence of dust or foreign matter and ice that has such imbedded therein. From careful conductivity tests it is found that the ice which is formed on the underside of a surface sheet growing over flowing water is as pure as it is possible to get anything in nature. Indeed Zsigmondy ("Colloids and the Ultramicroscope") recommends freezing as a means of producing clean water required in ultramicroscopic work. Samples of pure ice produce water which is contaminated only by the vessel into which they are placed. Bacteriological tests show ice to be absolutely sterile even when grown over polluted water. Every trace of foreign matter is eliminated by the slow freezing over the moving water.

It seems more than probable that Prof. Raman is correct, and that the color of ice is due to the large group molecules. In a similar way the color of the water is due to the light scattered by the ice molecules in solution. Iceberg ice is interesting because it shows no crystal structure is without cleavage lines, and appears to be what one would expect from the way it is formed. It is simply pressure ice, and consists of a mass of fine grains grown from the nuclear structure supplied by the snow and frost forms on the high interior plateau of Greenland. Pressed down into a compact mass after countless ages under great pressure, the bergs are finally launched forth to begin their journey southward. From the very nature of the internal structure of glacier or iceberg ice one would expect to find the deepest color.

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* Crystal Structure of Ice. Wm. Bragg, *Proc. Roy. Soc.*, 34, 98 (1922).

In the color of water it is difficult to separate the effect of fine impurities from the true molecular scattering. Glacier streams and lakes are always the bluest and appear to be deepest in shade when coldest. The water of the St. Lawrence River comes from the great lakes system which is a gigantic settling basin for the silt and mud, and its water is clear and blue wherever it is seen. It is a wonderful sight in winter to watch the varying shades as the temperature changes. There is a great similarity between a mass of ice and a mass of water just at the freezing point. I am not speaking of ice as we ordinarily know it, but I am thinking of water which has flocculated, and in which the particles have grown to large dimensions. Freshly formed ice is in the nature of a great clot, which undergoes structural alterations. The slowness of formation of ordinary river ice causes large crystals but when formed rapidly from water that is slightly supercooled the crystals possess fine colloidal structure.

Frazil Ice

A very beautiful example of flocculation is afforded by what we call in Canada *frazil.* This ice gives at times unlimited trouble to Power Companies, in that it accumulates at the intake, on the rack bars, or forms great hanging dams beneath the surface covering of the forebay. It packs in and obstructs the flow of the water like the slimy precipitates met with in chemical analysis. The manner of formation of frazil is quite simple. It occurs in open flowing water when at the freezing point, in long streamers and spongy masses and wide curtains which float low in the water and are easily carried along at considerable depths. The size of the particles are such as to give them, by Stokes' law,[3] little or no buoyancy. They have been mistaken for ice crystals heavier than water. The phenomenon is a true example of flocculation of a colloidal solution; the supersaturation is caused by the slight supercooling, and the flocculation follows probably as a natural consequence. The ice when it first forms is too fine to be seen by the eye apart from its action on the color of the water, but it soon agglomerates into the spongy masses of loose texture which readily catch onto objects in the water, and quickly build into the large masses.

As long as the temperature does not fall below 32° F. no frazil can form, but the smallest drop below causes it to appear. The balance is so delicate that it will escape detection by the most sensitive thermometer and the first indication that a drop has occurred will be the appearance of ice. Fig. 1 shows a microscopic photograph taken for me by Mr. W. A. Bentley last winter at Morrisburg, Ontario, of freshly formed frazil ice as it was taken from the river St. Lawrence on a cold morning in winter, before the sun has got high enough to influence the temperature of the water. The small well defined discs of ice can be easily seen and some of them are large enough to possess a more or less irregular crystalline form.

Later on, if allowed to grow on quiet water, they grow like snow crystals, but in running water they wear to hard lumps or spicules. This sometimes gives to an observer the impression of needle crystals and in fact the older name of frazil is "Needle" ice.

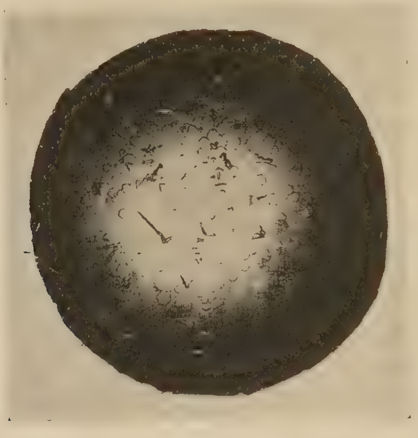

Fig. 1.—Microscopic photograph of Frazil ice freshly formed, showing small discs with no crystal shape. Magnification 2 diameters.

Anchor Ice

This form of ice grows on the bottom of the river wherever nothing protects the bed from excessive nocturnal radiation on cold clear nights.

Of all the ice on the upper St. Lawrence in the early winter anchor ice is the most abundant, and when released during the day forms by far the greatest bulk of the ice flowing down. It forms on points or rocks when the water is in a state of supercooling during the hours of 2 and 6 a. m. and sometimes attains a depth of five feet or more. It is of loose structure formed of large crystalline plates and is easily distinguished from frazil or snow blown into the water. Immediately on the advent of dawn, when the scattered radiation from the approaching sun glows in the eastern sky, the anchor ice begins to rise and floats in the stream. When the sun is actually up, and his rays are directed into the water, the bottom becomes quite clear of ice, until the following early morning hours when it grows again. Undoubtedly the deposition of ice comes from the contact of the supercooled water with the rocky bed, and the most copious growth takes place on the up-stream side of the rocks where the cooling would be most intense. During periods of intense nocturnal radiation, anchor ice is found abundantly, but on dull cloudy nights with high humidity no ice is produced.

Mist and Fog

Recent work on the nature of mist and fog is based on the nuclear theory. C. G. Simpson writes on this subject in a very clear way in a recent number of the *Scientific Monthly*,[4] when discussing atmospheric water forms.

Since water does not lose its trihydrol until well on to the boiling point, all evaporation at ordinary atmospheric temperatures releases a reasonable proportion of these ice molecules; but what happens during their free flight is not known. Moreover we do not know any more of the fate of the water particles. During very cold weather the ice molecules must persist and ultimately pass through molecular aggregation to the true crystal form of hoar frost. The finest colloidal particles in the atmosphere constitute the haze to be seen on a clear day over the sea, and finely divided sodium chloride forms a nucleus of a very persistent kind which is found many hundreds of miles inland from the sea. Compare Fig. 5.

The highest clouds consist of snow crystals and the presence of minute ice particles in the upper atmosphere is shown by the phenomena of sun dogs and moon dogs the positions of which with respect to the sun and moon prove the presence of solid particles which assume an hexagonal form.*

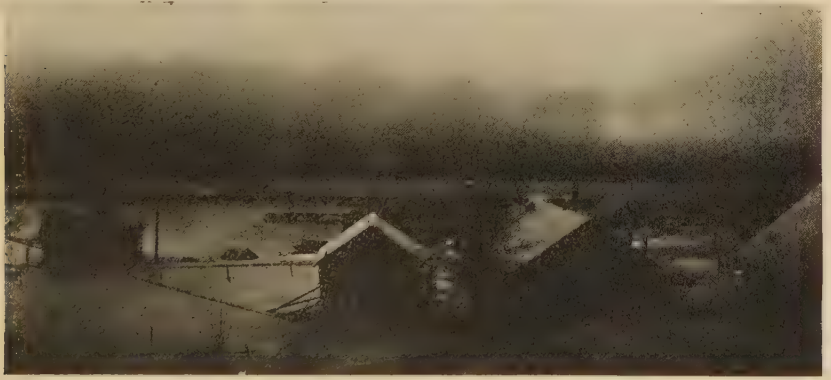

FIG. 2.—Black fog in the St. Lawrence River at Morrisburg, Ont. Dense white fog alone. Heavy shadow cast over all. No dust or smoke present.

Halos [5] are produced by colloidal particles of ice in the atmosphere, also the earth shadows which are plainly visible in the north. The white fogs over the sea may be produced by colloidal water particles, but the white fog formed on water surfaces when the temperature is very low (20 or 30 degrees below zero) is the most beautiful and fleecy cloud-like form that is known. The existence of the "white death" or "pogonip" of the Blackfoot Indians is caused by the excessive production of hoar frost resulting from a condition of unusual heavy precipitation of fine ice crystals. From their needle-like nature and their size they cause irritation to the lungs in the very cold weather, to which has been ascribed numerous outbreaks of pneumonia.

Probably the most interesting form of fog is the intense black fog which sometimes occurs during the very cold weather over the open surface of the St. Lawrence. Mists and winter fog are quite common over this river whenever the temperature goes below 11° F. The black fog occurs only at subzero temperatures and appears to be a heavy precipitation of semi-fluid globular particles which in their formation absorb completely the energy of the sunlight. It is preceded by a white fog, which, early in the morning, may rise to heights of 1200 feet in long streamers. With the rising of the sun the white fog subsides and the color changes to a sulphur yellow like burning saw-dust, and then rapidly to deep opaque black at the bottom. This shuts out completely all view of the water, of objects on the surface, and of the opposite shore. In Fig. 2 I show a photograph taken last winter of one of the thickest black fogs ever known on the river. Fig. 2 was taken at 9 a. m. just after the sun had driven the fog down, and shows the black blanket over the entire water surface between the edges of the border ice fields.

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* Prof. Keyes of McGill University informs me he has on several occasions measured the sun dogs as seen in Montreal. His angles are all consistent and the mean is 23°, 1½′.

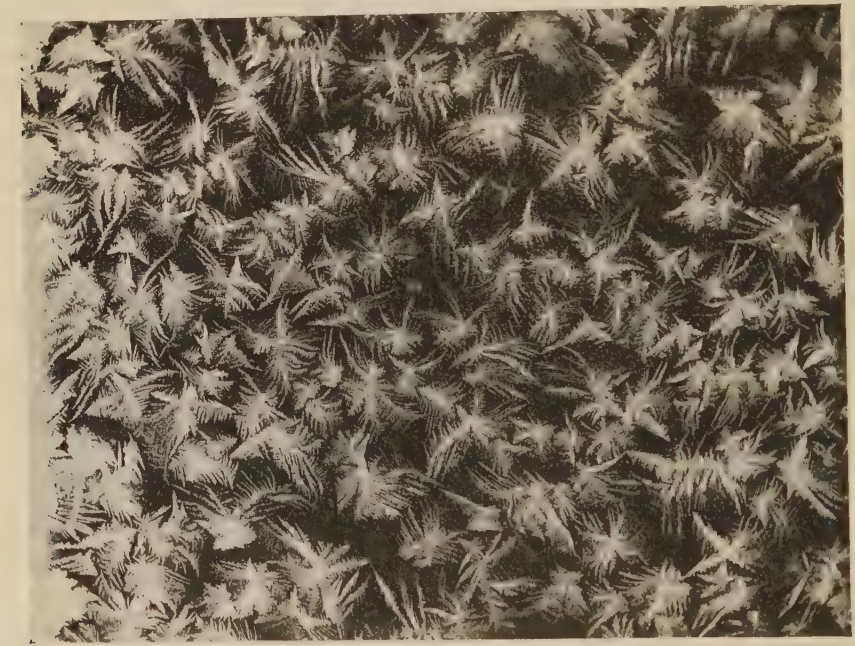

Fig. 5.—Colloidal ice. Odd window frost. Effect of traces of sodium chloride in the air.

On rowing out into this fog the temperature was much higher than the surrounding air and the blanket felt quite warm to the face, proving what an effective protection this fog is to the loss of heat from the water. The white fog can be readily seen to consist of plates and minute particles which are deposited along the shore on the grass and trees and give rise to some very beautiful sights.

Frost and Snow

Frost patterns on glass offer an interesting study of the influence of colloids on crystallization. In the window frost pictures reproduced here, which were taken last winter at Cornwall, Ontario, by W. A. Bentley, may be seen typical cases of colloidal protective influence on crystallization. Sodium chloride present in the atmosphere so far inland as Cornwall produces the characteristic four prong star shaped patterns,[6] Fig. 5.

The gradual alteration of form from the simple colloidal water particle deposited from the air on the glass, to the fully developed crystals is well illustrated in Fig. 3. The glass itself, being a colloid, affects the crystal form, and the impurities left on the glass after cleaning produce abundant evidence of colloidal protection. Fig. 4.

Many of Bentley's pictures show that a spherulitic phase, probably composed of groups of colloidal crystals made spherical by surface tension, precedes the formation of regular crystals and even of dendrites.

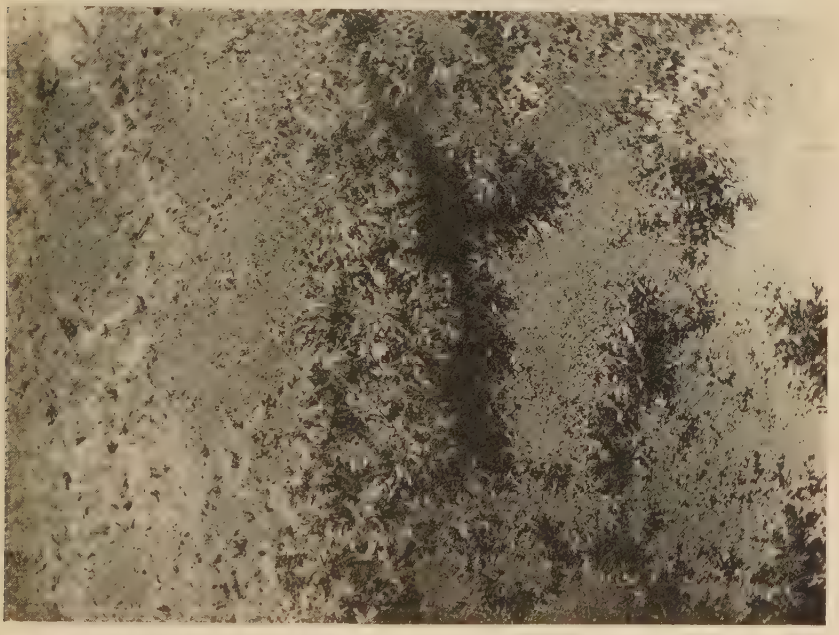

FIG. 3.—Young window frost showing crystals forming from colloidal deposits.

There are good instances of this in plates 13, 15 and 17, in Bentley's article in the *Monthly Weather Review* of 1907. Very little is known in regard to the cause of the varied shapes assumed by snow crystals, but undoubtedly we shall sometime have an explanation. The wonderful collection of varied forms which has been made by W. A. Bentley will prove of greatest help in a study of this kind.

It is of little use to speculate as to the origin of the snow crystal. Mr. Bentley has given his views of this phenomenon, but it is impossible to know what is the nature of the nucleus which is the stimulus for the growth.[7] The same nucleus which is active in causing the colloidal water forms in the atmosphere must be at the same time the generating influence of the solid. In the upper atmosphere we have abundant material in the form of ionized air and cosmic dust to produce the nuclei.

Colloidal Forms in Liquids

It has been pointed out that the moisture content of organic liquids results in the appearance of colloidal particles, and as an instance of this we have the colloidal water and ice in chloroform, which appear on cooling that material; but we are only at the threshold of our knowledge of the influence of colloidal water and ice. The molecular groups in water to which we have referred at the beginning of this paper are undoubtedly the basic nuclei for the many and varied forms.

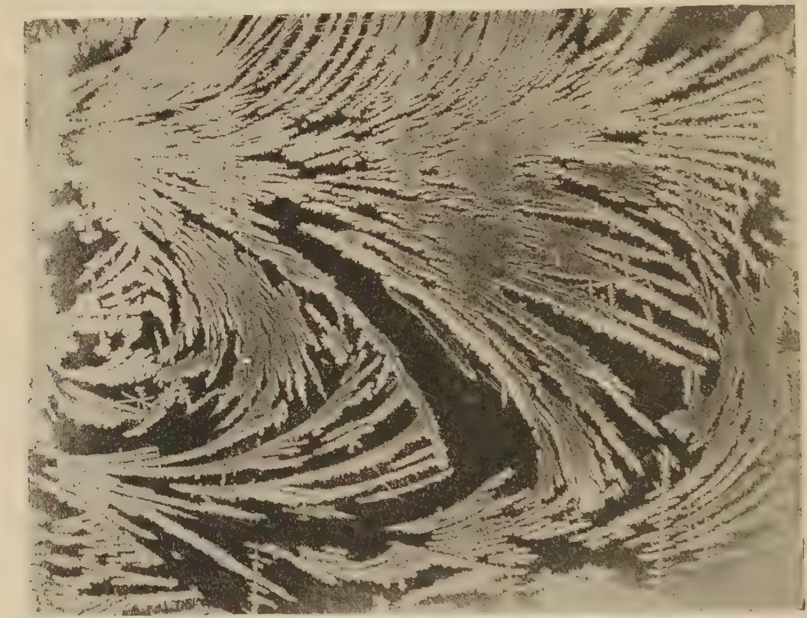

Fig. 4.—Colloidal ice. Window frost modified by effect of colloidal impurities (probably soap) left from the last cleaning process.

The influence of these liquid aggregates on chemical reaction and on crystal form has been completely overlooked in the past, but may easily be the real seat of the chemical activity of water.

In a future article will be shown some of the more important of the active properties of water in their relation to these liquid aggregates.

In conclusion it may be interesting to note the following from the works of Thos. Graham, F.R.S., published in 1861 to which my attention was drawn by Mr. Alexander.

"Ice itself presents colloidal characters at or near its melting point, paradoxical though the statement may appear. When ice is formed at temperatures a few degrees under 0° C., it has a well marked crystalline structure, as is seen in water frozen from a state of vapor in the form of flakes of snow and hoar-frost, or in water frozen from dilute sulphuric acid as observed by Mr. Faraday. But ice formed in contact with water at 0° C. is a plain homogeneous mass with a vitreous fracture, exhibiting no facets or angles. This must appear singular when it is considered how favorable to crystallization are the circumstances in which a sheet of ice is slowly produced in the freezing of a lake or river. The continued extrication of latent heat by ice as it is cooled a few degrees below 0° C., observed by Mr. Persons, appears also to indicate a molecular change subsequent to the first freezing.

Further, ice, although exhibiting none of the viscous softness of pitch has the elasticity and tendency to rend seen in colloids. In the properties last mentioned it suggests a distant analogy to gum incompletely dried, to glue or any other firm jelly.

Ice further appears to be of the class of adhesive colloids. The reintegration (regelation of Faraday) of masses of melting ice when placed in contact has much of a colloidal character. A colloidal view of the plasticity of ice demonstrated in the glacial movement will readily develop itself.

A similar extreme departure from the normal appears to be presented by a colloid holding so high a place in its class as albumen.

In the so-called blood-crystals of Funke, a soft and gelatinous albumenoid body is seen to assume a crystalline contour.

Can any facts more strikingly illustrate the maxim that in nature there are no abrupt transitions, and that distinctions of class are never absolute?"

McGill University,
November 25, 1925.

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5. Compare L. Besson, *Compt. Rendus*, **170**, 607 (1920).

6. The best example of this is given by Bentley, page 109, upper right-hand corner, in The Magic of Snow and Dew. *Nat. Geo. Mag.*, January, 1923.

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On reading Bentley's paper in the *National Geographic Magazine* (1923), I was struck by the fact that his beautiful photographs illustrated several colloidal principles. On writing him at Jericho, Vt., I received a copy of his paper in the *Monthly Weather Review* for , wherein I found reference to a book by Prof Barnes, who kindly consented to write up the subject, in which he has long experience. J. A.

Dispersed Systems in Astronomy

By Prof. Henry Norris Russell, Princeton, N. J.

A chapter on colloids in astronomy, in the stricter sense, would resemble the famous one upon the snakes of Ireland—there are none. Dispersed systems, of an extreme degree of density, indeed exist, on a grand scale, in interplanetary and interstellar space; but the particles are scattered, not in a medium of any kind, but in a vacuum far more perfect than has ever been attained by artificial means. In such a system, molecular attraction plays no sensible part and Brownian movement is replaced by motion in free paths, like that of the molecules of a gas.

Among the more noteworthy of these dispersed systems may be mentioned:

1. The Zodiacal Light. *

This faint luminosity in the sky extending along the ecliptic in both directions from the Sun, and moving around the heavens every year with the Sun, is generally recognized to represent the reflection of sunlight from a multitude of minute particles, forming a vast lenticular swarm, centered on the Sun, and extending beyond the Earth's orbit—so that the light which they scatter, though strongest near the Sun, extends over the whole sky and accounts for nearly one-third of the whole light of the sky on a moonless night.

The amount of material required to do this is minute. Jeffreys[1] shows that, if the light-scattering material is gas of properties similar to ordinary air, the mean density must be of the order 10^{-18} gm./cm.^{3}, while the mean free path of a molecule would be of the order of 10,000 kilometers—small enough to ensure that the assemblage, which is fully 300 million km. in diameter, could be treated as a gaseous mass.

If the particles of which the zodiacal light is composed are of more than molecular dimensions, their light-scattering power per unit of mass will be greater, and even these low estimates of density must be greatly diminished.

2. The Solar Corona.

This outer envelope of the Sun, so conspicuous at the time of a total eclipse, is also, in all probability, composed of particles which scatter sunlight. The unknown "coronium," which gives the green line in the spectrum, is clearly a minor constituent even in the inner corona, and absent in the outer regions. In this case it seems certain that the coronal matter must be in the gaseous state, for no solid or liquid particles could escape volatilization at the high temperature and low pressure which must prevail.

From the observed brightness, Jeffreys[2] estimates that the density is of the order of magnitude of 10^{-12} gm./cm.^{3} near the Sun's surface, and diminishes rapidly upwards.

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* See also paper of W. D. MacMillan, this volume. J. A.

3. Comets' Tails.*

Comets' tails afford still another example of a very conspicuous body of evanescent density. A multitude of phenomena indicate that they are composed of matter repelled strongly by the Sun—so that the tail always points away from the latter. From observations of "condensations" in the tail, which have sometimes been followed for nearly two days, and found to move with ever increasing velocity, it is clear that a comet's tail is rarely, if ever, so much as a week old. By that time the flying particles have dispersed so far that the stream of light fades away into the sky.

Spectroscopic observation shows that the luminous material of the tail is gaseous. Certain bands produced in carbon monoxide at very low pressure being predominant—though the bands of cyanogen, nitrogen, and the "Swan spectrum" of carbon appear in the head. Solid particles of diameters comparable with a wave-length of light, may also be present. These, like individual molecules, would be driven away from the Sun by radiation pressure. The density of the tail must be exceedingly low. Schwarzschild and Kron[3] from the observed brightness of the tail of Halley's Comet compute that the mean density must have been 2×10^{-21} gm./cm.^{3}, if the particles were 10^{-4} cm. in radius, and 4×10^{-24} gm./cm.^{3} if they were of molecular dimensions. In the latter case the mean free path would be 10^{19} cm.—comparable with the distances of the nearer stars.

4. Saturn's Rings.

Saturn's rings are known to be composed of particles which are small from the astronomical standpoint; but as there is definite photometric evidence that their particles are large enough to cast shadows on one another, and thickly enough packed (in the brighter portions of the rings) to occupy two or three per cent of the volume, the system cannot fairly be called either colloidal or dispersed.

5. Galactic Nebulae.

Hubble's work has made it quite clear that the brighter spiral nebulae at least are aggregations, not of tiny particles, but of stars; but the galactic nebulae, which lie at distances of thousands of light years (rather than millions) show good evidence of being dispersed systems. The immense dark nebulae which obscure the Milky Way in various regions appear to be clouds of matter, interposed between us and the more distant stars. It is easy to show that, for equal masses, fine dust, of diameter a few millionths of an inch, would be vastly more effective in forming such clouds than would either larger or smaller particles,† and it is very probable that such dust is mainly responsible for the obscuration. The dimensions of these clouds are measurable in light years. Their densities are probably very low. On the assumption that a dark cloud observed by Barnard is held together by its own gravitation, the writer has estimated[4] that the total mass is some 60 times that of the Sun. As the diameter of the cloud is of the order of a parsec (3×10^{18} cm.), its mean density comes out of the order of 10^{-20} gm./cm.^{3}. The luminous galactic nebulae, as Hubble has shown,[5] can in practically all cases be associated with bright stars, which appear to be the primary source of the luminosity. If the associated star has a lower surface temperature than that of spectral class B1 (probably about 20,000°) the nebula shows a continuous spectrum, if the star is hotter, a gaseous spectrum. In either case, the visible nebula appears to be a surface phenomenon—either a superficial illumination of a more extensive, and otherwise dark, nebula by the star's light, or a superficial fluorescence of the nebula, under the stimulus of its radiation.

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* See p. 25. Also J. Alexander, "Colloid Chemistry" (1924), p. 59. J. A.

† Escaping steam shows this well. J. A.

To sum up: Many exceedingly dispersed systems are revealed by astronomic observation, always by the property of absorbing light, scattering light, or emitting fluorescent light. In most cases the probable density is amazingly low—corresponding often to less than a single molecule per cubic millimeter—and the particles, whether of molecular or greater size, must be moving as independent bodies, with only rare collisions. Gravitation is the only known concentrating force; radiation pressure the principal known dispersive force. Though hardly colloidal in the proper sense, these systems present many unsolved problems for future study.

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On the variability and brilliance of the zodiacal light, see *e.g.,* letter by Chase S. Osborn, *Science,* Sept. 15, 1922, p. 308 (Vol. 56). J. A.

The Planetesimal Hypothesis

By Prof. W. D. MacMillan,
University of Chicago

About the beginning of the present century it was found by T. C. Chamberlin and F. R. Moulton, of the University of Chicago that the nebular hypothesis of Laplace as to the origin of our planetary system, which had been current, almost universally, during the nineteenth century, was seriously out of harmony with the evidence of geology and with the dynamical implications of astronomy. Laplace had appealed to the principle of rotational instability in the nebula which he supposed had condensed into our present sun. Rings were abandoned in the process of contraction and our present system of planets was formed from the break up of these rings. In 1854 Helmholtz showed that in this process of contraction sufficient heat would be generated to last the sun, at its present rate of radiation, for 20,000,000 years; and Helmholtz' contribution added greatly to the strength of the hypothesis of Laplace, so that it maintained its currency into the early years of the present century. The criticisms brought against it, however, seem to be fatal and it is now quite generally abandoned.

In offering the planetesimal hypothesis of the origin of our planetary system Chamberlin and Moulton have appealed to a new principle, namely, dynamic encounter of our sun with another star; not in the nature of a collision, but merely in a close approach. The expectancy of the sun for such a close approach is one in four million billion (4×10^{15}) years, if by the word "close" we mean the distance from the earth to the sun, one astronomical unit. With the ideas prevailing at the beginning of the present century as to the order of astronomical time (not exceeding perhaps one hundred million years) this small expectancy seemed to make the postulated encounter highly improbable, so that if it occurred it was highly accidental. It was only a decade, however, until the methods of radioactivity showed that in the oldest known geological strata there are rocks fifteen hundred million years old and therefore the earth is at least that old. The ideas as to astronomical time, too, have expanded enormously, so that what seemed highly improbable twenty-five years ago, now seems inevitable. The galaxy of stars is certainly many eons old, if by an "eon" we mean a million billion (10^{15}) years. In sufficiently long intervals of time the close approaches of stars become certainties.

Perhaps ten or twenty billion years ago our sun, then very similar to what it is today, passed close to another star; the two stars moving in hyperbolic orbits about their common center of gravity. Vast tides were raised upon the sun by the visiting star; the internal activities of the sun which are now manifested by sun spots and prominences were enormously stimulated so that streams of matter were ejected by the sun both in the general direction of the star and in the opposite direction. Most of this ejected material soon fell back upon the sun, some was ejected so far that it was lost to the system altogether, while a small portion equal to $\frac{1}{7}$ of 1 per cent of the total mass of the sun was deflected from its radial motion by the attraction of the visiting star, and commenced to move about the sun in highly eccentric orbits in the same direction in which the visiting star was moving. The duration of the star's "visit" was brief, perhaps a few months, and when it had passed on its way the sun returned to its original state, except for the matter which had been torn from it and which was circulating about it, all moving in the same general direction.

The ejection of this material was explosive in its nature, so that it was not uniformly distributed.* It was almost purely gaseous at the time of its ejection, so that, in accordance with the laws of gases, a rapid dispersion of it began save for a few large masses, from somewhat smaller than the earth and upward, in which the gravitational attraction was sufficiently strong to prevent gaseous dissipation. These larger masses served as nuclei for the sweeping up and gathering in of the free atoms and molecules and even larger masses which were incorporated into their own substance, and in the course of time developed into our present system of planets. In accordance with known dynamical principles this integration process diminished both the eccentricity of the orbits and their inclination to the plane of the visiting star, thus accounting for the main facts that all of the planets move in the same direction about the sun in orbits which are nearly circular and but little inclined to the plane of the ecliptic.

In the smaller masses the process of dissipation began at once, but the rate of dissipation was slower as the mass was larger. The delay in dissipation resulted in a process of condensation from a purely gaseous state to a mixture of gases and minute particles in a colloidal state. Colloids, however, do not obey the laws of gases, so that even with masses which were too small to resist gaseous dissipation there was left a residue which eventually consolidated with sufficient gravitative power to hold together and perhaps even to grow somewhat by the accretion of colloidal and solid particles drawn in from its neighborhood. This process accounts for the existence of the asteroids and other small bodies such as the satellites, which if reduced to a gaseous state would at once begin to dissipate.

The dissipated gases could not, however, escape from the control of the sun. They remained in its neighborhood, and notwithstanding their orbital motion about the sun, a process of atomic and molecular integration must soon have brought some of it to a colloidal state; a state which was helpful to the growth of the smaller bodies which could hold the colloids but not the gases. This differentiation is helpful in understanding why the smaller planets are conspicuously heavier than the larger ones. The process of sweeping up the gaseous and colloidal matter in the neighborhood of the sun, and therefore the growth of the planets, is essentially complete at the present time, the zodiacal light alone remaining as a witness of the past.

If two or more nuclei had been ejected simultaneously from the sun at about the same speed, the smaller ones would become the satellites of the larger ones, and this accounts well for the satellites of Uranus and Neptune and the forward moving satellites of Saturn and Jupiter. There is a possibility, in the early stages of the process, of the capture of asteroids and the conversion of them into satellites; and this may account for those satellites which have a backward motion and even for our own moon which is, in some ways, an extraordinary satellite.*

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* The eruptions of Krakatoa which filled the upper atmosphere with colloidal matter for some years and of Mt. Pelée (Martinique) where the *nuée ardente* caused such great loss of life, are mere Lilliputian outbursts. Nelson, State Geologist of Tennessee, estimates that a prehistoric volcano in his State spit up about 50 cubic miles of material. J. A.

The planetesimal hypothesis accounts well for the general features of our solar system and is in absolute conflict with none of them. It has the confidence of a large body of astronomers and geologists at the present time.

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* For further details see T. C. Chamberlin, *The Origin of the Earth;* F. R. Moulton, *Introduction to Astronomy.*

A more complete exposition of Prof. MacMillan's views, including mathematical treatment and a discussion of the regeneration of matter from energy in space, is to be found in *Science,* 1925.

Dr. Otto Struve, of Yerkes Observatory, has recently found evidence of finely divided calcium clouds, some forming an envelope of glowing stellar mist about a star system, others existing as free clouds without visible stars.

Prof. L. Vegard's view that the green color of the aurora borealis is due to the effect of solar emission on frozen nitrogen crystals floating above the atmosphere, was modified by Prof. J. C. McLennan, who showed that the color is probably due to a mixture of helium and oxygen. The existence of colloidal particles at such heights and at such temperatures, seems not improbable; and they conceivably have something to do with the so-called Heaviside layer and with the radio phenomena associated with it. J. A.

The Thermal Chemistry of Colloids

By Prof. Frederick L. Browne and Prof. J. Howard Mathews,
University of Wisconsin, Madison, Wis.

The quantitative study of the heat effects involved in the processes of solution has played an essential part in the theory of solution. In a similar way an accurate knowledge of the thermal changes accompanying colloidal phenomena is required for a thorough development of the theory of the subject. The earliest workers evidently realized this, for we find Selmi,[54] Graham,[55] and Linder and Picton [57] all remarking that little or no temperature change accompanies the peptization and coagulation of hydrosols of sulfur, Prussian blue, arsenous sulfide, and ferric oxide. For example, Graham says, "the phenomena of the solution of a salt or crystalloid probably all appear in the solution of a colloid, but greatly reduced in degree. The change of temperature usually occurring in the act of solution becomes barely perceptible."

In spite of the early interest in this branch of the subject, however, it has received very inadequate attention from the experimental standpoint and practically none from the theoretical. A number of scattered papers have been published on various phases of the problem but most of them belong to the older literature and are chiefly of historical interest because essential portions of the data are lacking. In particular the significant rôle played by the small amounts of soluble "impurities" present in the colloids has not been sufficiently appreciated until recently. The present chapter cannot pretend to cover the thermal aspects of colloidal behavior in a systematic way, but can only review the present state of our knowledge of the subject in the hope that it may provoke a more active pursuit of the necessary experimental evidence for which the development of the theory must wait.

The Heat of Wetting of Solids by Liquids

In 1822 Pouillet [1] observed that heat is evolved when finely powdered solids are wet by liquids, resulting in a rise in the temperature of the mixture. He used four liquids, water, oil, alcohol, and ether, with a wide variety of solids. With inorganic substances such as metals, oxides, glass, porcelain, silica, and sulfur he obtained temperature changes of 0.16° to 0.94°, while with organic materials such as carbon, starch, flour, grains, hair, cotton, silk, and animal membranes effects as great as 10° were produced. The different liquids showed no marked differences in behavior. He attributed the heat effects to physical phenomena connected with capillarity and ascribed the larger values with the organic substances to their greater surface. While this is probably true to a considerable extent we now know that with the latter, heats of swelling and of solution of soluble impurities played important parts.

The subject appears to have received little further attention for over thirty years until Tate [3] noted a rise in temperature of 5° when unsized

TABLE I

THE HEAT OF WETTING OF SOLIDS BY LIQUIDS

Solid	Liquid	Heat of Wetting	Observer	Year
Silica, well dried	Water	13.23 cal./g.	Ercolini[10]	1885
"	"	3.80	Meissner[11]	1886
" well dried	"	19.00	Martini[18]	1896
" " "	"	26.00	Bellati and Finazzi[16]	1900
"	"	0.616	Schwalbe[19]	1905
" 0.00025 cm. diam.	"	11.40	Parks[18]	1903
" 0.00040 " "	"	7.15	"	
" 0.0005 " "	"	13.80	Linebarger[17]	1901
" 0.00096 " "	"	6.90	"	
" 0.00175 " "	"	0.89	Parks[18]	1903
" 0.01 " "	"	0.24	"	
"	"	15.30	Gaudechon[21]	1913
"	Alcohol	14.70	"	
"	Amyl alcohol	13.50	"	
"	Acetic acid	13.50	"	
"	Ether	8.40	"	
"	CS_2	3.60	"	
"	Amyl alcohol	2.80	Meissner[11]	1886
"	Glycerine	0.80	"	
Silica gel	Water	19.22	Patrick and Grimm[25]	1921
" "	Alcohol	22.63	Patrick and Grimm	
" "	Benzene	11.13	Patrick and Grimm	
" "	CCl_4	8.42	Patrick and Grimm	
" "	Aniline	17.54	Patrick and Grimm	
Quartz sand	Water	0.00	Bouyoucos[23]	1918
Clay loam	"	2.98	"	
Silica	"	442.80	"	
"	Ligroin	97.20	"	
Clay	Water	12.60	Gaudechon[21]	1913
Silica, 0.0005 cm.	Nitrobenzene	11.21	Linebarger[17]	1901
"	Toluene	9.61	"	
"	Benzene	4.06	"	
"	Pyridine	11.84	"	
Charcoal	Water	7.425	Chappuis[9]	1883
"	"	14.23	Ercolini[10]	1885
" , animal	"	2.35	Meissner[11]	1886
" , sugar	"	3.90	Gaudechon[21]	1913
" , bone	"	18.50	Harkins and Ewing[26]	1921
Wood	Water	11.54 to 19.64	Dunlap[24]	1917
"	Creosote	5.02	"	
"	Turpentine	2.31	"	
Dextrin	Water	16.40	Sprockhoff[27]	1922
Magnesium oxide	"	1.60	Meissner[11]	1886
" "	Amyl alcohol	0.8	"	
Aluminum oxide	Water	1.16 deg. rise	Gore[12]	1894
Manganese dioxide	"	0.47 " "	"	
Ferric oxide	"	0.12 " "	"	
Barium carbonate	"	0.10 " "	"	
Lead oxide	"	0.08 " "	"	
Calcium sulfate	"	0.05 " "	"	
Barium sulfate	"	0.00 " "	"	
" "	"	13.50 cal./g.	Bouyoucos[23]	1918
" "	Ligroin	0.00	"	
Lead sulfate	Water	0.00	Koehler and Mathews[28]	1924

paper wrapped about the bulb of a thermometer was dipped in water. He concluded that "this change of specific heat which always takes place during the process of absorption is doubtless indicative of chemical action." The discussion concerning the causes of the heat of wetting thus started gave rise to a number of researches, but we are still very far from a complete understanding of the subject.

Some of the results obtained by different investigators have been collected and appear in Table I.

With the exception of the observations of Bouyoucos on silica the results of the different observers are reasonably consistent and show quite clearly that there is generally an evolution of heat when a solid is wet by a liquid. The magnitude of the heat effect varies both with the nature of the solid and of the liquid, being very small in some cases. The greater part of the heat effect is involved in the taking up of those first small portions of the liquid which are later removed with great difficulty. The heat of wetting is greater the greater the specific surface of the solid.

A number of theories have been advanced to account for the heat of wetting. We have already mentioned Tate's suggestion that chemical action takes place at the interface. Obviously this view did not prove very useful in dealing with so many substances between which no chemical reactions in the ordinary sense are known. Maschke[7] attempted to account for it on the basis of friction between the liquid and the solid and Meissner[11] agreed that this might explain it in part.

Rose[6] concluded that solids condense a layer of water under compression at their surface, from the fact that on determining the density by means of a pycnometer he obtained higher results the more finely divided the solid. This hypothesis was adopted by Jungk[4] to account for the heat of wetting as the heat of compression of this layer of adsorbed water. Since on compression water evolves heat above 4° and absorbs it below that temperature it follows that the heat of wetting at 0° should be negative. Jungk found this to be the case with sand and water. Following this view Melsens[8] computed the magnitude of the force of compression, using Regnault's values for the heat of compression. He found that the adsorbed water on charcoal is under a pressure of 893 atmospheres, alcohol 3080, ether 4620, carbon bisulfide 13090, and bromine 23100. Similarly Lagergren[14] found a pressure of over 6000 atmospheres for silica and water.

Meissner[11] objected to the compression theory because he found, contrary to Jungk's report, that the heat of wetting of silica with water is positive at temperatures below 4° as well as above. It was later pointed out by Parks,[18] however, that the temperature of maximum density of water falls to 0° at 200 atmospheres pressure; hence if the adsorbed film is under greater compression than 200 atmospheres the heat of wetting must always be positive. The reason for the apparent discrepancy in the observations of Jungk and of Meissner was found by Bellati[15] to be due to the fact that the latter used carefully dried silica whereas the sand used by the former probably contained a small amount of moisture to begin with. Bellati found that the heat of wetting of dry sand is positive at either 0° or 8°, but if the original moisture content is greater than 1.4 per cent it is positive at 8° and negative at 0°. These observations are in line with the compression theory if the adsorbed layer is more than one molecule deep and the pressure falls off rapidly from the surface to the normal pressure within the liquid.

Schwalbe[19] more recently studied the heat of wetting of sand with water at temperatures above and below 4°, finding a considerable evolution of heat at temperatures above this limit and no effect at 4°. When water was added to sand below 4° there was at first a slight evolution of heat, followed by a somewhat greater absorption so that the net effect was a slight negative value. To account for the preliminary warming he assumed that a layer of air is first imprisoned about the particles and compressed, causing the rise in temperature. When this air is displaced by water, the absorption of heat takes place. That this conception is not entirely impossible is shown by the observations of Masson[36] on the wetting of cotton wool, which will be discussed later on. Schwalbe also found that the largest portion of the heat effect is involved with the first portions taken up and rapidly falls off to zero when a certain proportion of water has been taken up. The amount of water required for the complete development of the heat effect varied widely with different sands, from 0.15 gram water per gram of sand in one case to over 1.8 gram in another. This he ascribed to differences in the specific surface.

Lamb and Coolidge[40] have recently had much success with the compression theory in explaining the heat of wetting of charcoal by various vapors and find that the pressure on the adsorbed liquid is of the order of 37,000 atmospheres.

Martini[13] was unwilling to admit pressures of several thousand atmospheres in the layer of water adsorbed on silica and instead adopted the solid solution theory first proposed by Cantoni.[5] He reasoned that just as solids are dissolved by liquids and thereby become liquid, so water may be dissolved by silica and thereby become solid. The heat of wetting is then the heat of solidification of the water. More recently Bouyoucos[23] has also adopted this point of view. He found that the heats of wetting of a large number of soils parallel the amount of water retained by the soil which fails to expand as though freezing when cooled to — 78°. The latter measurements were made in the dilatometer. Both the heat of wetting and the amount of water failing to freeze increase with the colloidality of the soil. He therefore concluded that a part of the water in the soil is in the solid state to begin with.* Beadle[33] and Masson[36] regard the water absorbed by cotton wool as being held in solid solution. Masson computed that the water film, if held at the surface, would be $15 \cdot 10^{-5}$ cm. thick, which seemed unreasonable to him.

But Bellati[15] showed, by direct determination of the specific heat of silica containing varying amounts of water from 8 to 25 per cent, that the water present always has a specific heat of 1 instead of 0.5 as would be expected if it were in the solid condition.

The solid solution theory does not indicate any connection between the heat of wetting and the specific surface of the solid, whereas with either the compression theory or the surface energy theory, to be discussed later, the heat of wetting must be greater the greater the specific surface. Martini[13] stated that with silica and water the fineness of the powder is without influence on the result. More careful studies by Linebarger[17] and by Parks,[18] however, showed that the heat effect is greater with finer particles. Their results are given in Table I. Parks' results are probably the more reliable and merit further consideration. They are given in greater detail in Table II.

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* If the compression theory is correct and the adsorbed water is much more dense than water at one atmosphere pressure, Bouyoucos' calculation of the amount of water freezing from the contraction in volume would be in error in such a direction as to indicate that less water had undergone a change in state than was actually the case.

TABLE II

Heat of Wetting per Unit of Surface Area

Kind of Silica	Specific Gravity	Diameter of Particles, cm.	Area of Surface per G. SiO_2	Heat of Wetting	
				Per G. SiO_2	Per Cm.² Surface
Precipitated	2.2	0.00025 cm.	10,900 cm.²	11.40 cal.	0.00105 cal.
"	2.2	0.00040	6,820	7.15	0.00105
Sand	2.6	0.010	231	0.24	0.0010
Glass wool	2.7	0.00175	874	0.89	0.0011

He found the heat of wetting to amount to 0.00105 calories per sq. cm. of surface for particles varying 40 times in relative size. The heat of wetting of glass wool was the same as that of silica. In this case he computed that the heat effect is confined to a layer of water $13.3 . 10^{-6}$ cm. thick because 3.37 grams took up 0.0388 gram water from saturated aqueous vapor and thereafter showed no heat of wetting on submerging in water.

Bellati and Finazzi[16] studied the heat of wetting of samples of silica having varying moisture content, obtaining the results given in Table III, columns (a) and (b). The computations of columns (c) to (f) were made by Parks, basing them upon his determination of the heat of wetting per cm.² of surface as given in Table II. It will be seen that the heat effect falls off rapidly as the thickness of the adsorbed layer increases. This would be expected on the basis of the compression theory since we should expect the pressure to vary from a maximum immediately at the interface to 1 atmosphere at the outside of the adsorbed layer.

TABLE III

Heat of Wetting of Silica of Varying Moisture Content

(a) Per Cent	(b) Cal./G.	(c) Calories	(d) Cal. × 10^{-6}	(e) Cal. × 10^{-4}	(f) Cal./Cm.²/Cm.
0.00	(26) extrapolated				
2.38	18.29	7.71	0.95	3.08	325.0
5.35	12.33	13.77	2.14	5.51	258.0
8.59	9.17	16.83	3.44	6.73	185.0
12.92	7.61	18.39	5.17	7.36	142.0
18.83	6.50	19.50	7.53	7.80	106.0
27.36	5.25	20.75	10.94	8.30	75.8
39.95	3.70	22.30	15.98	8.92	55.8
46.35	2.94	23.06	18.54	9.22	49.7
56.48	1.66	24.34	22.59	9.74	43.0
64.78	0.90	25.10	25.91	10.04	38.6
76.94	0.19	25.81	30.78	10.32	33.6

(a) Percentage of water in the silica.
(b) Observed heat of wetting, calories per g. silica.
(c) Heat evolved when dry silica takes up the amount of moisture indicated in column (a), that is, 26-(b).
(d) Thickness of film of adsorbed water. The total surface is computed by taking the heat of wetting of dry silica from Table II to be 0.00105 cal. per cm.², whence for this silica 26/0.00105 gives 25000 cm.² per g. The thickness of the water film is therefore 0.01(a)/25000.
(e) Heat evolved per cm.² of surface, (c)/25000.
(f) Heat evolved per cm.² of surface by a film 1 cm. thick, (e)/(d).

Parks also found that when glass wool is immersed in mercury, heat is absorbed. This is not surprising as wetting does not take place in this case, so that the most important factor to consider is the extension of the surface of the mercury.

Koehler [28] and Mathews found that there is no heat effect during the wetting of lead sulfate with the saturated aqueous solution. The specific surface of the lead sulfate varied from 5,842 to 32,400 cm.^{2} per gram. Lead sulfate seems to be much less readily wet by water than by oils because it was found that if the material was washed with laboratory distilled water which was known to contain minute traces of lubricating oil it could not be satisfactorily wet on submerging in water. Other lead compounds behave similarly, for example in the manufacture of basic carbonate white lead the water is displaced from the pulp lead on adding the linseed oil.

Gaudechon [21] considers the heat of wetting to be due to association or polymerization of the molecules of the liquid in contact with the solid. In support of this view he cites his data for the heat of wetting of silica, clay, starch, and charcoal with 16 liquids. He found a very rough parallelism between the heat of wetting and the constant K in the Eötvös formula and LM/K of the Pictet-Trouton relation. Apparently those liquids such as water and the alcohols which readily associate give high values for the heat of wetting. It should be noted that this apparent relationship would hold if we consider the heat of wetting to be due to changes in the surface energies of the system.

As we have already mentioned, Pouillet held that the heat of wetting is a surface phenomenon connected with capillarity. However, until within the last few years no further attention has been paid to this point of view except for a passing comment by Meissner.[11] The latter dismissed the surface consideration with the remark that the increase in the surface of the water would absorb heat instead of evolving it, forgetting that at the same time the large potential energy of the solid-air interface is replaced by the solid-liquid interface.

Patrick and Grimm [25] have considered the heat of wetting of silica gel from the standpoint of the surface energy changes involved. They distinguish between capillary adsorption and adsorption on a plane surface. The initial film of adsorbed liquid is admitted to be under compression, but is held to be negligible in amount as compared with the total condensation in a solid having capillary structure. The silica gel contained several per cent of water and is believed to consist of an agglomeration of silica nuclei, each particle being surrounded with an envelope of water. Therefore the gel is regarded as exhibiting an enormous water surface which is the seat of considerable energy. When this material is immersed in water the surface mentioned above disappears, due to the fact that a water-water interface cannot exist. When, on the other hand, the gel is wetted by a liquid such as benzene the total surface undergoes no diminution in area, but the surface energy is greatly decreased due to the diminution of the interfacial tension. At the same time an amount of heat is set free equivalent to the decrease in surface energy, thus accounting for the heat of wetting.

Patrick and Grimm obtained the following values for the heat of wetting of silica gel with liquids:

Water	19.22 calories per g.
Ethyl alcohol	22.63 " " "
Benzene	11.13 " " "
Carbon tetrachloride	8.42 " " "
Aniline	17.54 " " "

The total surface energy of the water interface is

$$E = \omega\sigma - T\frac{d\sigma}{dt} = 117.08 \text{ ergs per cm. at } 25^\circ.$$

The surface that one gram of gel must possess to account for the heat of wetting on the basis of this theory is therefore

$$\omega = \frac{19.22 \times 4.182 \times 10^7}{117.08} = 6.9 \times 10^6 \text{ cm.}^2$$

Zsigmondy observed particles of the order of 5 $\mu\mu$ in silica gel. If the density of the gel is 2 the surface of 1 gram would be

$$\frac{3 \times 0.5}{2.5 \times 10^{-7}} = 6 \times 10^6 \text{ cm.}^2$$

which agrees very nicely with the theory. In a similar way it is computed that the total surface energy of 1 cm.^{2} of a water-benzene interface is 51.66 ergs, hence the heat of wetting by benzene is 117.08 — 51.66 or 65.42 ergs per cm.^{2} Assuming the above value for the surface area of the gel the heat of wetting per gram is

$$\frac{65.42 \times 6.9 \times 10^6}{4.128 \times 10^7} = 10.74 \text{ calories,}$$

agreeing with the value of 11.13 calories observed. For carbon tetrachloride the calculated value is 7.10 as compared with 8.42 observed and for aniline 16.56 compared to 17.54 observed. The high value of the heat of wetting with alcohol is not so satisfactorily accounted for, but the authors promise to give more attention to it in a future publication.

Harkins and Ewing[26] have obtained direct experimental evidence of the compression of the layer of liquid adsorbed on a solid in the case of activated charcoal and organic liquids. They find that the apparent density of the charcoal as determined in the presence of the various liquids varies very widely. No relation between the apparent density and the size of the molecule of the liquid or the ratio of the surface tension to the viscosity of the liquid was found, hence it is concluded that the discrepancies cannot be explained on the ground of differences in the completeness of filling of the finest capillaries by the liquids. Since the apparent density increased in the order of increasing compressibility of the liquids it seems evident that the liquids are compressed at the interface. The attractive force between the charcoal and the various liquids is shown to be constant and of the order of 30 or 40 thousand atmospheres, in agreement with the findings of Lamb and Coolidge.[40] It is pointed out that experiments on the internal pressure of liquids have not succeeded in demonstrating pressures higher than 72 atmospheres.

Harkins and Ewing derive the heat of adsorption of a liquid by a solid from surface energy considerations as follows. If we consider that the solid is immersed in the liquid in such a way as not to increase materially the surface of the liquid against air (or more strictly against its vapor), the net result is that the surface of the solid is replaced by a solid-liquid interface. The heat of adsorption, $-Q_a$, is then equal to the total amount of energy given off in the process when carried out isothermally, E_a, or

$$-Q_a = E_a = E_s - E_i$$

where E_s and E_i are respectively the total energies of the solid surface and of the interface. Since, further, the total energy of a surface is equal to the free surface energy, γ, plus the latent heat of the surface, $-T\frac{\partial\gamma}{\partial T}$,

$$-Q_a = \gamma_s - T\frac{\partial\gamma_s}{\partial T} - \gamma_i + T\frac{\partial\gamma_i}{\partial T}.$$

The heat of adsorption of a liquid on a solid has always been found to be positive, indicating that the total surface energy of the solid is greater than that of the interface. For the adsorption of one liquid by another it is also generally found that the heat effect is positive, but there are cases in which it is negative.

The total adhesional energy is always greater than the energy of adsorption and may be expressed as

$$-Q_A = E_A = E_s + E_l - E_i$$

since in this case we consider the surfaces of the two phases to be already in existence before contact is made, and both surface energies vanish and are replaced by the interfacial energy. Likewise the heat of spreading of a liquid over a solid, whereby the solid surface disappears to be replaced by a solid-liquid interface plus a liquid surface, is given by

$$-Q_{sp} = E_{sp} = E_s - (E_l + E_i).$$

The heat of adsorption of a saturated vapor is

$$-Q_g = E_s - E_i + \lambda v$$

where $-Q_g$ is the heat of adsorption of enough vapor to form a liquid in bulk covering the solid surface at constant temperature, and λ is the latent heat absorbed in the vaporization of the liquid per unit volume of vapor and v the volume of vapor adsorbed. It is assumed here that the area of the surface of the liquid formed is negligible in comparison with the area of the interface.

The equation for the heat of adsorption or heat of wetting derived by Harkins and Ewing, as described above, permits of an interesting deduction regarding the temperature coefficient of the heat of wetting.

$$-Q_a = \gamma_s - T\frac{\partial\gamma_s}{\partial T} - \gamma_i + T\frac{\partial\gamma_i}{\partial T}$$

$$\frac{d(-Q_a)}{dT} = \frac{d}{dT}\left(\gamma_s - T\frac{\partial\gamma_s}{\partial T}\right) - \frac{d}{dT}\left(\gamma_i - T\frac{\partial\gamma_i}{\partial T}\right)$$

$$= -T\frac{\partial^2\gamma_s}{\partial T^2} - T\frac{\partial^2\gamma_i}{\partial T^2}.$$

Now for a liquid not too close to its critical temperature $\frac{\partial^2\gamma_l}{\partial T^2} = O$, since the $\gamma_l - T$ curve is a straight line. If the same is true for the $\gamma_s - T$ and $\gamma_i - T$ curves,

$$\frac{d(-Q_a)}{dT} = O$$

and the heat of wetting is independent of the temperature.

HEAT OF ADSORPTION OF VAPORS BY SOLIDS

De Saussure[29] in 1814 first observed that heat is evolved when boxwood charcoal, which had been previously heated to redness and cooled under mercury to exclude air, is allowed to adsorb various gases.

It has long been recognized that a large part of the heat evolved during the capillary adsorption of vapors by porous solids is the heat of liquefaction of the gas. That the adsorbed vapor exists in the liquid state is indicated in the first place by the large volume condensed and in the second place by the fact that the heat of adsorption always exceeds the heat of liquefaction. This is illustrated by the data of Favre[30] given in Table IV. The values given in parentheses are supplied by Bancroft ["Applied Colloid Chemistry," p. 26].

TABLE IV

HEAT OF ADSORPTION OF GASES

Adsorbent	Gas	Heat of Adsorption Cal. per Mol. of Gas	Heat of Liquefaction Cal. per Mol. of Gas
Platinum	Hydrogen	46,200	(240)
Palladium	Hydrogen	18,000	(240)
Charcoal	Ammonia	5,900– 8,500	(5,000)
"	Carbon dioxide	6,800– 7,800	6,250 (includes solidification)
"	Nitrous oxide	7,000– 7,700	4,400
"	Sulfur dioxide	10,000–10,900	5,600
"	Hydrogen chloride	9,200–10,200	(3,600)
"	Hydrogen bromide	15,200–15,800	(4,000)
"	Hydrogen iodide	21,000–23,000	(4,400)

In the cases of hydrogen on platinum and palladium the heat effects recorded by Favre are probably due in part to oxidation by traces of oxygen that cannot be readily removed. The above values are for the heat liberated when the adsorbent takes up the gas to saturation. The heat effect is greater for the first portions taken up than for the last, indicating that the first portions are held under greater compression than the last, according to Favre.

Chappuis[32] obtained results quite in agreement with those of Favre. He pointed out that the excess heat effect over that required for liquefaction is the heat of wetting as observed by Pouillet. Titoff[38] more recently obtained similar results and Dewar[35] found similar conditions to hold at — 185°.

Lamb and Coolidge[40] have made an extensive investigation of the heat of adsorption of a number of vapors on activated charcoal at 0° and find that the heat effect may be represented by the equation

$$h = mx^n$$

where h is the heat of adsorption per gram of charcoal, x the volume of vapor adsorbed, and m and n are constants. Their results are given in Table V.

There is a close parallel between the value of $1 - n$ and the boiling point of the liquid. For gases far from the boiling point the heat of adsorption per unit amount of gas adsorbed decreases only slightly as the adsorption proceeds, but with gases near the boiling point it falls off more rapidly.

Lamb and Coolidge regard the heat effect as due to two factors, the heat of liquefaction of the gas and the heat effect due to further compression of this liquid by the adhesive forces of the adsorbent. The latter, or net heat

TABLE V

HEAT OF ADSORPTION OF VAPORS BY CHARCOAL

Liquid	n	m	h_m Kg. Cal.	H_m Kg. Cal.	H_m per C.C.	P_1 1000 Atm.	P_2 1000 Atm.
C_2H_5Cl	0.915	0.7385	12.33	6.11	0.0864	8.5	27.5
CS_2	0.9205	0.7525	12.63	5.80	0.0991	13.5	30.2
CH_3OH	0.938	0.742	12.95	3.62	0.0908	12.0	28.9
C_2H_5Br	0.900	0.900	14.33	7.48	0.1020	11.9	29.2
C_2H_5I	0.956	0.737	14.25	6.44	0.0815	11.0	26.1
$CHCl_3$	0.935	0.8285	14.93	6.93	0.0875	12.3	—
$HCOOC_2H_5$	0.9075	0.944	15.42	7.04	0.0901	10.3	—
C_6H_6	0.959	0.774	15.17	7.36	0.0850	11.5	—
C_2H_5OH	0.928	0.871	14.98	4.33	0.0768	11.6	28.2
CCl_4	0.930	0.893	16.09	8.09	0.0856	11.3	—
$(C_2H_5)_2O$	0.9215	0.917	16.09	9.19	0.0803	8.3	26.9
NH_3	0.695	2.23	13.4	2.87	0.105	—	—

(Data for NH_3 taken from Chappuis.)

of adsorption, is equal to the heat of wetting at the saturation pressure of the liquid. In the fourth column headed h_m are given the values for the molecular heat of adsorption when 1 c.c. of the *liquid* is adsorbed by 10 grams of the charcoal. Subtracting the molecular heats of vaporization leaves the values for the net molecular heats of adsorption, H_m, for 1 c.c. of the liquid adsorbed by 10 grams of charcoal. It will be seen that these are of the same general order of magnitude as the heats of vaporization. When the net molecular heat of adsorption is divided by the molecular volume of the liquid at 0° we obtain the net heats of adsorption per c.c. of liquid, H_m per c.c. These values are nearly the same for all the liquids. The heats of compression of the liquids can be computed from the thermal dilatation. When the net heats of adsorption per c.c. are divided by the heats of compression per atmosphere per degree we get the force of compression, P_1, under which the liquid exists in the adsorbed layer. These prove to be reasonably constant. If we use the experimentally determined values of the heats of compression up to 12,000 atmospheres, obtained by extrapolating Bridgeman's results, we arrive at the much more accurate pressures P_2. These prove to be more nearly constant. This is still not quite accurate as the pressures prove to be greater than the 12,000 atmospheres which is the limit of Bridgeman's data. The actual compression must be about 37,000 atmospheres, as nearly as can be estimated. The thickness of the layer of adsorbed gas is shown to be many molecules deep, so that we are dealing with capillary adsorption rather than mono-molecular adsorption.

Williams[39] derived an expression for the heat of adsorption from the Clapeyron equation in the following manner. If λ_p is the heat evolved per gram mol of gas adsorbed at constant pressure p and temperature T, and Δv is the difference in the volume of gas before and after adsorption,

$$\lambda_p = \Delta v T \left(\frac{dp}{dT}\right)_a = RT^2 \left(\frac{d \log p}{dT}\right)_a,$$

where a is the number of cc. of gas at normal temperature and pressure adsorbed by one gram of adsorbent at the pressure p. Now if P is the saturation pressure of the adsorbed vapor in liquid form, λ_P is the heat of condensation of a gram mol of vapor at P and T, and ΔV the difference in volume of a mol of gas and liquid. Then

$$\lambda_P = \Delta VT \frac{dP}{dT} = RT^2 \left(\frac{d \log P}{dT} \right)$$

Hence if liquid were adsorbed the corresponding heat would be:

$$\lambda = \lambda_p - \lambda_P = RT^2 \left(\frac{d \log p/P}{dT} \right)_a$$

In the experiments of Lamb and Coolidge the heat of adsorption was composed of two factors of similar order of magnitude, the heat of condensation of the vapor and the "net heat of adsorption." In the case of the adsorption of vapors by cotton wool the first factor only seems to be of importance, the second being relatively very small. Beadle [33] first noted that cotton cellulose becomes very much warmer than its surroundings while it is absorbing moisture from damp air and concluded that the heat effect is due chiefly to condensation of the water, but also in part to the formation of a solid solution of the water in the cellulose. Masson [36] studied the phenomenon in greater detail. He wrapped dry cotton wool about the bulb of a thermometer and immersed it either in water or in air saturated with water, finding that the temperature rose rapidly to a maximum within 2 or 3 minutes in water or 5 or 6 minutes in air saturated with water vapor, falling off continuously thereafter for many hours as the cotton continued to take up water. The maximum temperature was found to be higher and was attained in a shorter time the higher the initial temperature of the cotton and the air. The cotton under water presents a glistening appearance because it retains an air film about the particles which is essential for the phenomenon. If medicated cotton is used, from which the natural wax has been extracted, the amount of air retained is very much less, and as a result the rise in temperature is much less. If ordinary cotton is submerged in absolute alcohol or if glass wool is submerged in water, in which cases no air is retained, the heat of wetting is too small to be detected under the conditions of the experiments. The heat effect is easily observable, however, when the cotton is placed in air saturated with alcohol vapor or glass wool in moist air. The heat effect in these latter cases is due chiefly to liquefaction of the water vapor or, in the immersion experiments, to distillation across the air film. In the case of glass wool in moist air there is involved only a local transfer of heat, which would not be noted in calorimetric experiments. The facts that the heat effect is proportional to the amount of moisture absorbed and amounts to 0.57 calories per milligram of water, in agreement with the computed value of 0.576 calories liberated when one milligram of water vapor at 25° condenses to liquid at 37.7° (the conditions of the experiment), confirms this view. Masson agrees with Beadle that the water is held in solid solution in the cellulose because the amount condensed if adsorbed at the surface would make a film 15×10^{-5} cm. thick, which is very much thicker than Parks [18] found for the water film on glass.

In the adsorption of vapors by charcoal the heat effect per gram of gas adsorbed falls off as the adsorption proceeds. We are dealing in these cases with capillary adsorption in which the adsorbed film is many molecules thick. Favre[30] found similar conditions to hold true in the adsorption of hydrogen by platinum and palladium, but his results are rendered inaccurate by failure to remove all the oxygen held by the metals. Mond, Ramsay and Shields [34] carefully removed all traces of oxygen from their adsorbents and found a value of 13,800 calories per gram mol for the adsorption of hydrogen by platinum, much lower than the results of Favre. Moreover, they found that the heat effect was the same for the last portions taken up as for the first. Beebe and Taylor[42] have recently reported results for the heat of adsorption of hydrogen by nickel, finding values varying from 13,500 to 20,500 calories per mol depending upon the previous history of the adsorbent. As the latent heat of vaporization is only about 450 calories per mol it is evident that condensation is not the important factor. The heat effect was the same for the last portions taken up as for the first. With copper as adsorbent the heat of adsorption was found to be 9,600 calories per mol. It appears, therefore, that in the adsorption of gases by metals we are generally dealing with monomolecular adsorption.

THE HEAT OF SWELLING

When the elastic gels such as gelatin, agar, starch, etc., take up water and swell there is a marked evolution of heat. The heat of wetting of wood observed by Dunlap[24] may be due in whole or in part to this and it entered into some of the experiments of Duvernoy,[58] to be mentioned later. Wiedeman and Lüdeking first measured the heat of swelling for several substances, finding it positive for all the gels studied, including gelatin, gum arabic, dextrin, and starch. Their work is of historical interest only, however, since the moisture content and purity of their materials are uncertain. Pascheles[45] likewise noted that heat is evolved during swelling of a large number of substances in water and in glycerine. His materials were washed thoroughly to free them from soluble impurities, but the moisture content is still unknown.

Rodewald[46] and Rodewald and Kattein[47] found that in the swelling of starch by water the heat effect depends upon the original moisture content, the largest amount of heat being evolved during the adsorption of the first portions of water and then rapidly falling to zero at a moisture content in the neighborhood of 30 per cent. The results can be expressed in the form of the equation

$$cw = \log (r_0 + i) - \log (r + i)$$

where r_0 is the heat of swelling of dry starch, r that of starch with the moisture content w, and c and i are constants. The results shown in Table VI were obtained with different starches.

TABLE VI

HEAT OF SWELLING OF STARCH

Kind of Starch	i	c	Moisture Content Above Which Heat of Swelling Is Zero
Rice	2.53	0.0407	26.79 per cent
Wheat	1.39	0.04231	31.63
Arrowroot	2.49	0.0371	29.99
Soluble	1.01	0.0349	43.44
Potato	2.94	0.02889	37.10
Artificial	2.95	0.0298	36.12

The contraction in total volume during swelling was found to be proportional to the heat effect.

Rosenbohm[49] made a similar study with gelatin. The dry material evolves 36.0 calories per gram, on swelling. By measuring the heat effect with gelatin of varying moisture content and subtracting each value from 36.0, data were obtained for plotting the heat effect when dry gelatin takes up increasing amounts of water. The curve rises linearly to about 32 calories at 22 per cent, then more slowly until all the measurable heat has been evolved at 50 per cent, although swelling is not complete until 1100 per cent water has been taken up. The following values for the heats of swelling of other dry materials were observed:

Agar	35.5	calories	per	gram
Cellulose (filter paper)	9.6	"	"	"
Cellulose (pure)	12.9	"	"	"
Cotton	20.8	"	"	"
Hair	17.0	"	"	"

Rosenbohm concluded that the heat of swelling is not due to capillary absorption but is analogous to the heat of hydration of salts. Freundlich ["Kapillarchemie," ed. 1920, p. 506] considers that the data support the view that the heat effect is due to adsorption of water by the gelatin, similarly to the heat of wetting, because the heat effect parallels the volume contraction.

Katz[48] plotted curves for the heat of swelling, vapor tension, and volume contraction as functions of the amount of water taken up for such gels as cellulose, casein, wood fiber, and gelatin and showed that they are analogous to the corresponding curves for miscible liquids such as water with sulfuric acid, phosphoric acid, and glycerine. He concludes therefore that amorphous swelling substances differ from liquids only in viscosity and that swelling is due to the formation of a solid solution of water in the imbibing substance.

Laurie and Ranken[50] found that when shellac is boiled in borax solution a gel is formed which swells greatly on placing in cold water. Careful experiments failed to disclose any heat effect accompanying the swelling, but the authors pointed out that the heat of swelling might have been counterbalanced by a negative heat of solution of inorganic impurities.

Knoevenagel[51] found that the heat of swelling of acetyl-cellulose per mol divided by the moles of liquid or liquid mixture imbibed is a constant and is the same for alcohol, alcohol-benzene, and nitrobenzene as swelling liquids. The value is 0.111 Kg. calories per mol.

HEAT OF ADSORPTION FROM SOLUTION

Gore[52] has made an attempt to study this subject in the case of silica and solutions of inorganic salts. He noted qualitatively that the introduction of the dry silica into the solution decreases the concentration of the salt in the remaining solution and is accompanied by an evolution of heat. The heat effect is sometimes less than that with pure water and sometimes more, indicating that the heat of adsorption, which is the difference between the observed heat effect and the heat of wetting, may be positive or negative.

Kruyt and van der Spek[65] added moist charcoal to solutions of crystal violet and measured both the heat effect and the amount of adsorption with the following results:

Charcoal Gms.	Heat Change Calories	Adsorbed Dye Mgs.	Heat Effect Cal. per Mol. Adsorbed	Remarks
5.0	16.58	2.21	7,500	Solution not decolorized
5.0	16.94	2.01	8,430	" " "
5.0	16.13	1.54	10,500	Solution decolorized
5.0	15.94	1.54	10,300	" "

Heat of Coagulation

The earliest workers in the field of colloid chemistry noted that, in contrast to true solutions, little or no change in temperature is to be observed during the formation or coagulation of colloidal solutions. Selmi,[54] Graham,[55] and Linder and Picton [57] all made such observations, although in a later publication Graham [56] records a rise in temperature of 1.1° during the coagulation of silica sol by powdered charcoal. The heat effect may have been due to the wetting of the charcoal.

The first very careful investigation was made by Wiedeman and Lüdeking [61] who concluded that "the solution of dry colloids consists of two processes, (1) hydration with evolution of heat, (2) solution with absorption of heat." Thus, when 2 grams of gelatin were swollen in 10 c.c. of water at 18.4°, 11.4 calories were evolved. When this gel was then raised to 34° and enough water added to form a sol, 7.4 calories were absorbed. Similar results were obtained with gum arabic, dextrin and starch. They found that heat is absorbed on dissolving the crystalline forms of cane sugar and tartaric acid, while with the amorphous forms heat is evolved. Duvernoy [58] had previously made similar observations. Wiedeman and Lüdeking further found an evolution of 12 calories per gram when silica sol is coagulated with ammonia. The sol contained large amounts of electrolytes, however. Similarly, with egg albumin they found an evolution of heat on swelling, absorption on solution, and evolution on coagulation with acetic acid.

Thomsen [59] failed to confirm Wiedeman and Lüdeking's results with silica sol. He found the heat of neutralization with sodium hydroxide to be the same whether he started with the sol or with the gel. On spontaneous coagulation of the sol in the calorimeter he found no heat change. Similarly Berthelot [60] observed no heat effect during the coagulation of colloidal ferric oxide.

Frank [64] plotted the time-temperature curve for the cooling and gelation of a gelatine sol and found no change in the slope during the transformation, from which he concluded that there is no heat effect accompanying the change.

Prange [62] prepared a silver sol by the Carey Lea method which contained relatively large amounts of electrolytes. On coagulating this with ammonium nitrate solution he obtained an evolution of 251 calories per gram of silver with a sol containing 1 gram of silver in 2.179 liters of water and 127 calories with a sol containing 1 gram of silver in 0.2258 liters. Correction was made for the heat of dilution of the ammonium nitrate but not for its heat of mixing with the electrolytes already present. The latter effect would be ample to account for the observed heat evolution. The coagulated silver was then washed free from electrolytes and dried. This is a bluish-black powder which on treatment with dilute mineral acids is changed to the ordinary gray metallic powder. This transformation was found to involve an evolution of 60 calories per gram.

Leighton and Mudge [69] find that during the coagulation by heat of the casein in whole milk or in skim milk there is a marked absorption of heat at the instant when visible curd appears which may lower the temperature 0.05 to 0.1°. By using artificial skim milks, however, it was found that the presence of calcium and magnesium salts is necessary for this heat effect and that citrates and phosphates also influence it. The heat effects are considered to be due to separation of calcium and magnesium citrates and phosphates from the solution during coagulation, the calcium and magnesium previously held by the casein entering into this reaction. The absence of heat effect during the precipitation of pure calcium caseinate is pointed out also by Gayda.[66]

Fricke,[68] after showing on the basis of a number of theoretical considerations that the heat of coagulation of hydrosols must be very small, explains the heat effects observed by other workers on the basis of the electrolytes present in the sols they used.

Doerinckel [63] carried out an elaborate study of the heat of coagulation of ferric oxide and silica sols with various electrolytes. His sols contained considerable quantities of electrolytes, however, as shown by the analyses. In all cases he found an evolution of heat of the order of 100 calories per gram equivalent of ferric oxide. The magnitude of the heat effect was found to depend to a very large extent upon the concentration of the precipitant and upon its nature, and to be relatively greater for dilute than for concentrated sols. The heat effect was roughly proportional to the amount of precipitant adsorbed during the coagulation; but although the adsorption increased on continued standing of the coagulum in contact with the liquid, the heat effect was complete with the first coagulation. Although he found that sols containing less electrolytes gave a lesser heat effect, he apparently attached little significance to this fact. In making his computations he made corrections for the heat of dilution of the coagulant, but did not consider the heat of reaction of the electrolytes in the sol with those in the coagulant. The dilution of the sol gave no heat effect.

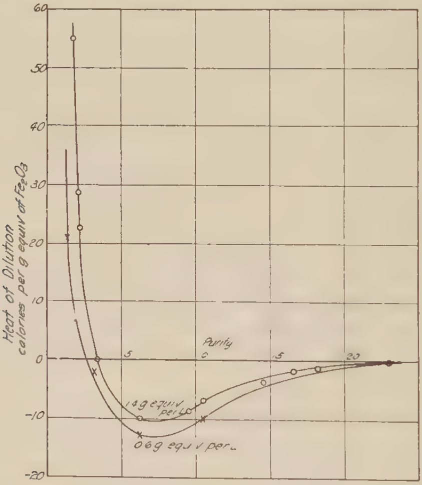

Fig. 1.—Heat of dilution of ferric oxide sols containing respectively 1.4 and 0.6 g. equiv. Fe_2O_3 per liter plotted as a function of the purity. 360 cc. of the sol were diluted with 255 cc. of water.

Doerinckel also found a positive heat of mutual coagulation of ferric oxide sol and a silver sol containing a protective colloid of unstated nature. The ratio of the amounts of the two sols required for the maximum heat effect, did not coincide with the ratio for maximum precipitation. No heat effect accompanied mixing of the ferric oxide sol and the protecting colloid. Coagulation of the silver sol with ammonium nitrate gave a small positive heat effect while with aluminum sulfate there was a slight negative effect. With the aluminum sulfate solution the protecting colloid gave a marked negative heat effect.

Kruyt and van der Spek [65] found that no measurable heat effect accompanies the coagulation of arsenous sulfide sol with potassium chloride or aluminum sulfate. With ferric oxide sol, however, they obtained an evolution of heat checking closely with Doerinckel's results. They too noted that the effect is less the lower the content of electrolytes in the sol. They noted also that there was an increase in volume during coagulation but no change with arsenous sulfide. They considered four possible sources of heat effect during coagulation: (1) adsorption of the ions of the coagulant, (2) change in interfacial energy due to decrease in the dispersion, (3) reactions between electrolytes in the sol and in the coagulant, (4) change in the hydration of the colloid particles. They concluded that the first would be compensated by the giving up of ions previously adsorbed by the particles in the sol condition. The second, assuming an interfacial tension of the order of 10^3 ergs per square centimeter for arsenous sulfide, would be considerable if much change in interfacial area takes place during coagulation. The absence of heat effect was therefore taken as proof of the view that there is not much change in dispersity in the first stages of coagulation at least. The third was excluded on the basis of the small amount of electrolyte present in the arsenous sulfide sol and it was concluded that the heat effect with ferric oxide was due to its emulsoid character and the change in hydration during coagulation.

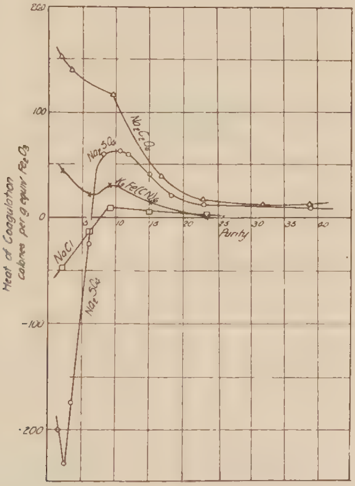

FIG. 2.—Heat of coagulation of ferric oxide sols containing 1.0 g. equiv. of Fe_2O_3 per liter with different electrolytes plotted as a function of the purity of the sol. 360 cc. of the sol were mixed with 255 cc. of the coagulants.

Browne and Mathews [67] made an extended investigation of the heat of coagulation of ferric oxide hydrosol with several electrolytes, taking into consideration the influence of the peptizing electrolytes in the sol. An adiabatic calorimeter was employed which made it possible to determine the heat effect within at least one calorie per gram equivalent of ferric oxide present. The sols were prepared by adding ammonium carbonate solution to ferric chloride and dialyzing, portions being withdrawn at intervals for the experiments. In this way sols containing varying amounts of peptizing electrolyte were obtained. The electrolyte content was expressed by the ratio of equivalents ferric oxide to equivalents chlorine present, and was referred to as the "purity," for convenience.

It was found in the first place that, contrary to the statements of previous workers, there is a marked heat effect accompanying the dilution of the ferric oxide sols of a purity less than 23, although the sols used by Doerinckel and by Kruyt and van der Spek had a much lower purity than this. Fig. 1 shows the heat of dilution of sols having a concentration of 1.4 and of 0.6 gram equivalents ferric oxide per liter, respectively. It will be seen that the heat effect is positive at very low purities, then becomes negative, and finally approaches zero. The heat of dilution of solutions of ferric chloride is likewise found to be positive at fairly high concentrations and to become negative as the dilution increases. When the heat of dilution is plotted against the concentration of chlorine for ferric chloride and the ferric oxide sols, curves of very similar shape and magnitude are obtained, indicating that the heat effect on diluting the sols is due to the electrolytes present.

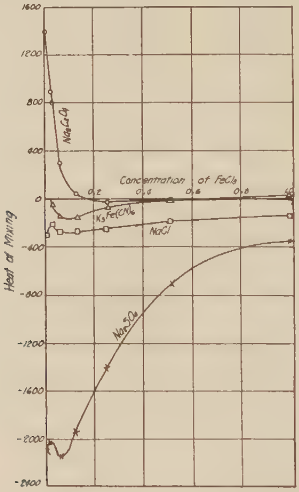

FIG. 3.—Heat of mixing of 255 cc. of the electrolyte solutions used as coagulants with 360 cc. of ferric chloride solution of varying concentration.

In computing the heat effects on coagulation of the sols with electrolytes, the heats of dilution of the sol and of the electrolyte were deducted. When this is done we find that the heat effect on coagulation of a ferric oxide sol containing 1.0 gram equivalent of ferric oxide per liter with various electrolytes varies considerably with the purity of the sol, as shown in Fig. 2. At low purities the heat effect may be positive and fall off rapidly at very high purities, soon falling within the experimental error. This points very strongly to the peptizing electrolytes of the sol as the source of the heat effects during the coagulation. This view is further strengthened by reference to Fig. 3 which shows the heat effect on mixing the coagulating electrolytes with solutions of ferric chloride of varying concentration. Fig. 4 shows the heat of coagulation with different concentrations of the coagulants. In each case coagulation took place at some concentration between the points marked A and B. The shape of the curves and the position of the coagulation point at such an inconspicuous part of the curve indicate that the coagulation of the sol has no bearing on the production of the heat effect.

This work seems to show quite conclusively that there is no heat effect accompanying the coagulation of the ferric oxide sol, and that the effects observed are due entirely to the electrolytes present. Ferric oxide therefore does not differ from arsenous sulfide in its thermal behavior on coagulation, the absence of heat effect with the latter being due to the greater purity of the sols employed and the nature of the peptizing electrolyte.

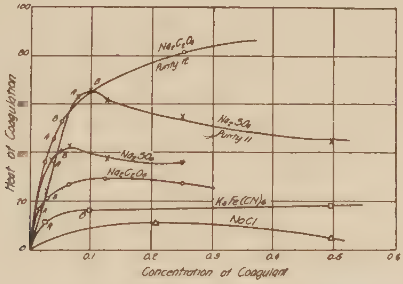

FIG. 4.—Heat of coagulation of ferric oxide sols containing 1.3 g. equiv. Fe_2O_3 per liter with varying concentrations of electrolytes. Except where stated otherwise the purity of the sol was 15. The limiting concentrations for the electrolytes lies between the points marked A and B.

Before the above conclusions could be checked quantitatively it was necessary to determine the amounts of ferric chloride and of hydrochloric acid in ferric oxide sols of different purity. Browne[70] accomplished this by means of measurements of the chlorine ion activities in the sols, using the concentration cell method. It was found that below a purity of about 14 the dispersion medium contained both ferric chloride and hydrochloric acid, while above this purity it contained neither ferric ion nor hydrogen ion, but still contained notable amounts of chloride ion. In other words, the ferric oxide adsorbed the ferric and hydrogen ions completely, but not quite all the chloride ions. These observations also were checked by the behavior of the sol on dialysis.

These sols were prepared by the addition of hydrogen peroxide to ferrous chloride solution and subsequent dialysis, in order to avoid the production of ammonium chloride as a by-product. Finally, Browne[71] determined the heat of coagulation of such sols with sodium sulfate solution, applying corrections for the heats of dilution of the sols and of the coagulant and for the heats of mixing of the sodium sulfate with the hydrochloric acid and the ferric chloride present. This gave the data of Table VII.

TABLE VII

Heat of Coagulation of Ferric Oxide Hydrosols

360 c.c. of the sol containing 0.66 g. equiv. Fe_2O_3 per liter coagulated with 255 c.c. 0.2 *N* sodium sulfate solution.

	Heat of Coagln. Corrected for		H_r			
Purity of Sol	Diln. Cal.	Mixing Cal.	Heat of Coagln. per G. Equiv. Fe_2O_3	$\frac{H_r}{Ad_{total}}$	$\frac{H_r}{Ad_{Cl}}$	$\frac{H_r}{Ad_{SO_4}}$
4.44	—53.6	47.4	200	1700	1700	4400
9.11	— 6.3	47.7	200	3100	1700	4400
13.00	11.1	51.1	216	2700	2200	2800
17.10	5.3	35.3	149	1700	1700	1800
27.20	2.1	22.1	93	2700	2300	4900
47.50	0.0	13.0	55	3100	1700	4400
			Ave.	2500	1900	4100

The first column gives the purity of the sol, the second the heat effect on coagulation corrected for the heats of dilution of the sol and of the coagulant, the third column the heat effect corrected also for the heats of mixing of the sodium sulfate with the ferric chloride and the hydrochloric acid in the sol, the fourth column this heat effect calculated per g. equiv. of Fe_2O_3 in the sol. When the supernatant liquid after coagulation was analyzed for chloride and for sulfate it was found that some sulfate had been adsorbed and some chloride previously held by the ferric oxide had been given up. The values in the fourth column divided by the sum of these changes in ion adsorption give the figures in the fifth column. It will be seen that these values are reasonably constant at 2500 calories per g. equiv. change in adsorption. A better way to make the calculations is to take the data for the different sols in pairs and set up simultaneous equations with the heats of adsorption of sulfate and of chloride as unknowns and solve for these quantities. The values in the sixth and seventh columns were obtained in this way. It will be seen that the heat of adsorption of chloride ion under these conditions is about 1900 calories per g. equiv. chloride and the heat of adsorption of sulfate about 4100 calories.

The evidence seems conclusive that the heat effects observed during coagulation of ferric oxide hydrosols with electrolytes are to be attributed entirely to the heats of dilution and of interaction of the electrolytes in the sol and in the coagulant and to the heat effect accompanying the changes in ion adsorption during the process. The change in dispersity of the ferric oxide from that characteristic of the sol to that of the coagulum does not involve a heat change measurable by our present methods. Moreover, Kruyt and van der Spek's suggestion that the heat effects with ferric oxide sols are due to their emulsoid characteristics is untenable. Either there is no change in hydration during coagulation or this change does not involve a heat effect.

Browne[72] has also shown that the heat effect accompanying the coagulation of sulfur sols is zero when the amounts of electrolytes present are not sufficient to involve measurable heat effects. This was found to be true even in sols containing particles under 30 μμ in diameter.

It seems to be true in general that during the coagulation of hydrosols no appreciable heat changes are involved provided the amounts of electrolytes present are not too great. This can be possible only if the interfacial tension is very small or if there is very little change in specific surface during coagulation. It is very probable that the latter is true and perhaps the former also. After the first stage of the coagulation there is reason to believe that in some cases a secondary change sets in whereby the specific surface decreases. It would be of interest to determine whether this process is accompanied by a heat effect, but the calorimetry involved presents difficulties inasmuch as the change takes place so very slowly.

THERMOCHEMISTRY OF PROTEIN SYSTEMS

Mathews[73] and Rowland have recently obtained important fundamental thermochemical data relative to the question of whether colloidal proteins react stoichiometrically with electrolytes, or whether, as colloidal suspensions, the proteins exhibit the properties of selective adsorption characteristic of colloids in general.

These investigators mixed hydrochloric acid solutions with dilute solutions of gelatin and of glycine respectively at 40° C. and measured both the heat evolved and the change in hydrogen ion concentration. With the simple amino acid glycine, 13,140 calories were evolved per gram equivalent of hydrogen ion removed by combination with the glycine. The simple neutralization of an acid by a base would be expected to give some such value. With gelatin, however, only 10.1 calories were evolved per gram equivalent of hydrogen ion bound. On mixing gelatin with a variety of acids, bases, and salts, the heat effects per gram equivalent of hydrogen or hydroxyl ion bound varied from 0 to nearly 8000 calories. The magnitude of the heat effect apparently depends neither upon the amount of hydrogen or hydroxyl ion bound nor upon the specific electrolyte employed but rather upon the p_H of the resulting solution, because on plotting all the data on a single graph with logarithms of the heat effect vs. p_H of the solution a smooth curve resulted, having a value of 0 at the isoelectric point of gelatin and maxima on the acid and basic sides. They concluded that gelatin does not enter into stoichiometric chemical combination with acids and bases, but exhibits selective ion adsorption. The similarity of the relation between heat effect and p_H on the one hand and the corresponding relations for viscosity of gelatin sols and swelling of gelatin gels on the other indicates that the heats of mixing observed are due to changes in the degree of hydration of the gelatin rather than to the adsorption of ions.

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Electric Phenomena in Colloid Chemistry

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Within the domain of theoretical electricity there exist a series of phenomena, evidently related to one another, whose connection with other electrical phenomena was for a long time not clearly demonstrated. It is noteworthy that the shorter textbooks of experimental physics treat them only superficially or even omit them altogether. Only by degrees have their relationships to the broader domain of electric theory become clear. It is these phenomena which form the basis of this chapter on "electric phenomena in colloid chemistry." Hence, for the historical development of the subject, it is desirable first of all to describe them. Following a suggestion of H. Freundlich, they are fittingly termed *electro-kinetic phenomena.* Their characteristic feature is that in a heterogeneous system, having at least one liquid phase, relative mechanical motion occurs between the different phases under the action of an externally applied electric potential; or, conversely, if relative motion occurs at the phase boundaries as the result of a mechanical force, a potential difference is set up in the direction of this motion. These phenomena are firstly *electro-endosmosis* and *cataphoresis*—these two being the mechanical effects of an external electric force; and secondly *streaming potential* and the *potential of falling particles* (migration potential)—phenomena which are the electrical effects of mechanical motion.

2. Endosmosis, Physically Considered

By the expression "physically considered" is meant that endosmosis, after being described first qualitatively as a physical phenomenon, will be treated quantitatively only insofar as it is dependent upon changes of a physical nature—such as external potential differences, degree of porosity, etc.,—and not insofar as concerns chemical changes in the substances under consideration. This mode of presentation is in accord with the historical development of the subject, and, furthermore, is advantageous because the dependence of endosmosis on the chemical nature of the substance under consideration is of the greatest importance in colloid chemistry, and, on account of the complicated nature of the relationships involved, can be grasped only with a knowledge of the purely physical phenomena as a prerequisite.

Endosmosis was discovered by Reuss[1] in the year 1809. If two tubes filled with water are thrust into moist clay and an electric current led in through metallic electrodes, water will rise in the tube containing the cathode and fall in that containing the anode. In 1816 Porret[2] described the phenomena again, as met in the sand filter, and subsequently the same, or converse, phenomenon *cataphoresis* (to be described later) was observed in various substances by Becquerel, Armstrong, Daniel, Faraday, E. Dubois Reymond, Heidenhain, and Jörgensen. Exact physical measurements were made by Wiedemann[3] and especially by Quincke. Whereas up to this time the question had this simple aspect, viz., that the water was carried along with the current—Quincke[4] showed that there were also cases in which the water migrated in the reverse direction. In order to explain the phenomenon, he assumed that the solid walls of the capillaries possess an electric charge with respect to the water, and that the surface of the water carries an equal charge but of opposite sign. This *electrical double-layer,* the source of which was unexplained, forms the essence of the later physical theory; endosmosis was explained henceforth by assuming that under the action of an externally applied potential the two components of this double layer move in opposite directions, each dragging along the particle or substance to which it is attached. The theory of endosmosis was first stated quantitatively by Helmholtz;[5] we re-state it in a form due to Perrin.[6] The experimental arrangement is as follows: A diaphragm, consisting of some solid material having channels of capillary dimensions, is inserted in a tube filled with liquid. Let us assume first the simple condition that the diaphragm consists of a single, cylindrical capillary. Further, assume that an electrical double layer exists at the boundary between the capillary wall and the liquid, of such a nature that the negative charge, say, is bound tightly to the wall of the capillary, while the positive charge lies a very small, but finite, distance, δ, from the wall—in the liquid—and hence is movable. If a potential difference is applied to the ends of the capillary, the two components of the double layer will move relatively to each other, that on the liquid actually moving, while that on the tube remains physically fixed. On account of friction, a constant speed of endosmosis will quickly be reached (as in the case of ion migration in electrolytes). In this equilibrium condition the electric force will be exactly equal to that required to overcome friction; the electric force, E, acting on unit surface of the capillary wall will be equal, then, to the frictional force, R. This affords the basis for the calculation of the potential difference, ζ, of the electrical double layer. The *electric* force, E, which is exerted on unit area of the bounding surface, is equal to the product of the charge, e, of the double layer, by the externally applied potential difference, H; that is,

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* Translated by W. G. Horsch, Ph.D., Scarsdale, N. Y. Prof. Michaelis gives here a general review of the basic theory.

$$E = eH. \tag{1}$$

The force of friction, R, since we have assumed that the motion takes place in the water, is equal to the product of the friction coefficient of water, η, the friction surface area—which is taken equal to unity—and the decrease, Δ, in velocity in a direction perpendicular to the wall of the capillary; that is,

$$R = \eta\Delta. \tag{2}$$

The following approximation may be made regarding the velocity-decrease, Δ. The velocity right at the capillary wall is zero. It increases, approximately linearly—reaching its maximum, u, at a distance, δ, equal to the thickness of the double layer. At greater distances the water is carried along at the same velocity, u, as a result of friction. Assuming, therefore, uniform variation in velocity within the double layer, the decrease, Δ, is given by the expression,

$$\Delta = \frac{u}{\delta}.$$

This decrease holds solely within the region of the double layer; beyond this region there is no velocity decrease. Hence, substituting in (2) we obtain,

$$R = \eta\left(\frac{u}{\delta}\right). \tag{3}$$

The velocity, u, may be measured in the following manner. Since the volume occupied by the double layer is a ring of such small dimensions as to be negligible compared with the total volume of the capillary, the *maximum* velocity of the water, u, is consequently equal to its *mean* velocity. As the result of endosmosis, a volume of water, v, flows out in unit time, which is equal to

$$v = \pi r^2 u \tag{3a}$$

where r is the radius of the capillary. Substituting the resultant value of u in equation (3) we obtain,

$$R = \frac{\eta v}{\delta \pi r^2}.$$

This friction force must equal the electric force (1), whence,

$$eH = \frac{\eta v}{\pi \delta r^2}. \tag{4}$$

In order to calculate the potential difference between the two layers from the electric force, the double layer is considered as an electrical condenser of potential, ζ, in a medium (water) of dielectric constant, D. Whence, according to a law of theoretical physics,

$$\zeta = \frac{4\pi\delta e}{D}$$

$$\text{or, } \pi\delta = \frac{\zeta D}{4e}.$$

Substituting in equation (4),

$$eH = \frac{\eta v 4e}{\zeta D r^2}$$

$$\text{or } v = \frac{r^2 \zeta H D}{4\eta} \tag{I}$$

$$\text{and } \zeta = \frac{4v\eta}{r^2 H D} \tag{II}$$

If, now, the diaphragm consists of a multiplicity of capillaries of combined cross section, q, then πr^2 will be replaced by q, or r^2 by $\frac{q}{\pi}$, whence,

$$v = \frac{q\zeta H D}{4\pi\eta} \tag{Ia}$$

$$\text{or } \zeta = \frac{4\pi v \eta}{q H D} \tag{IIa}$$

in which v represents, as previously, the water transferred in unit time. For the derivation of these equations a whole series of assumptions have been made which need not necessarily be true or whose truth cannot be demonstrated with certainty. First, we shall see presently that there can be no exactly defined value of δ, because double layers are not mathematical surfaces, but possess a diffuse boundary. Furthermore, it is not obvious that it is permissible to use as friction coefficient that of water, because conditions at the interface are not necessarily those of ordinary water. Our assumption is based, rather, on the preliminary view—not yet demonstrated in every instance—that δ is so large, that the properties of ordinary water may be ascribed to a water layer moving under the influence of an electric force. The same holds true also for the dielectric constant which has been taken simply as that of water. v. Smoluchowski raised the objection also that a diaphragm cannot be considered as a simple bundle of *straight-line* capillaries; the effect of this objection is slight, however, as he calculated.

If E is the electric potential applied to the ends of the diaphragm, and l its length, then $H = \frac{E}{l}$, and

$$v = \frac{q\zeta DE}{4\pi\eta l}. \tag{III}$$

If the potential drop between electrodes is E, and the resistance of the diaphragm is w, then according to Ohm's law, $E = iw$. This gives

$$v = \frac{q\zeta Diw}{4\pi\eta l}.$$

Since for diaphragms of the same chemical and physical properties and the same cross-sectional area, $\frac{w}{l}$ is a constant quantity, it follows that, for diaphragms of the same sort and the same area the quantity of water transferred depends solely upon the magnitude of current. Since the quantity of water transferred must increase with increasing cross-section, and since the current likewise is proportional to the cross-section, it follows for diaphragms of any length, breadth and thickness, provided they are physically and chemically alike, and also of course provided the aqueous solution has the same composition, *that the quantity of water transferred in unit time varies with the current only, and is proportional to it.*

Throughout the foregoing, it was presupposed that no hydrostatic head was developed as a result of the transference of the water, in other words, that the transferred water simply flowed out. If this is not the case and the transferred water rises, then equilibrium, a description of which possesses no special interest for our present purpose, will be reached at a certain pressure.

3. CATAPHORESIS

In the course of some endosmosis experiments with clay membranes, Reuss found that the fine particles of clay which occasionally became loosened from the membrane moved through the water under the influence of the current, but in the opposite direction from that in which water was driven through the diaphragm. This phenomenon is *electro-cataphoresis* or *electrophoresis.* It is simply the reverse of endosmosis. The building up of the electrical double layer cannot be due to the capillary structure of the interface but evidently is due to the boundary surface or interface itself. The movement of the water described in the previous section is to be considered as relative only; if fine particles are freely suspended in water, then cataphoresis occurs instead of endosmosis.

The theory of cataphoresis may be presented most simply, perhaps, in the following manner. Assume that a solid body of great length and very small diameter is suspended in water and that a potential difference is applied lengthwise of this body. Assume movement of the water to be impossible; this can be arranged either by completely enclosing the water by walls on all sides, or by placing the water in an open U-tube. In the latter case a slight rise in one arm as the result of endosmosis is the most that will occur and this quickly comes to rest, so that the water thereafter does not move and only the cataphoretic motion of the solid particle takes place. Then, under equilibrium conditions, the electric force, eH, acting on unit surface of the solid particle, will be that required to balance the friction force, $\eta\Delta$. Here again Δ is equal to $\frac{u}{\delta}$, whence

$$eH = \frac{\eta u}{\delta}$$

and, therefore,

$$u = \frac{eH\delta}{\eta}. \qquad (7)$$

According to the formula for potential of a condenser,

$$\zeta = \frac{4\pi\delta e}{D}$$

or

$$e = \frac{\zeta D}{4\pi\delta}. \qquad (7a)$$

Substituting in the previous equation

$$u = \frac{\zeta DH}{4\pi\eta}$$

or, solving for ζ,

$$\zeta = \frac{4\pi u\eta}{DH}.$$

From this formula and the speed of cataphoresis, the potential of the double layer may be calculated. In this calculation—as in the case of the earlier formulæ—it must be remembered that ζ is obtained in absolute units, provided the potential difference, H, which occurs in the right hand term, is also expressed in absolute units. If we write with primes the two quantities characteristic of the electric potential, thus ζ' and H', when they are expressed in volts, then, since 1 absolute unit = 300 volts.

$$H = \frac{H'}{300} \text{ and } \zeta' = 300\ \zeta.$$

Then

$$\zeta' = 300\left(\frac{4\pi u\eta}{DH}\right) \text{ absolute units}$$

and

$$\zeta' = (300)^2\left(\frac{4\pi u\eta}{DH'}\right) \text{ volts.}$$

Expressing this in words: in order to convert to volts the value of ζ calculated with the aid of equation 7a, it is necessary to multiply ζ by 90,000.

It is evident from formula 7 that cataphoretic velocity is independent of the size of the solid particle. Thus far a long narrow particle only has been considered and its orientation has been assumed parallel to the current filaments. It remains to be seen whether the relationships developed apply also to any given kind and shape of particle. Assume a spherical particle of *non-conducting* material. The lines of force of the electric field will not be straight in the immediate vicinity of the surface of the sphere, but will bend around it. The potential difference between the two ends of the particle, therefore, is greater than when the particle is long and narrow; the electric force acting upon it is greater, but the force of friction likewise is greater in proportion. The two influences counteract each other, whence it follows in general that the velocity of cataphoresis is independent not only of the size but also of the shape of the particle. If non-precipitable asymmetric particles give rise to deviations, it is of little consequence, because these are of no practical importance.

If the cataphoresis experiments are conducted in a fairly large tube (at least several millimeters in diameter) the theory is satisfied. However, if the space is very narrow, as is true of microscopic cells, complications are introduced, to provide for which v. Smoluchowski's theory was developed. Suppose the cell to have a length, between electrodes, of several centimeters, and a depth, on the other hand, of a fraction of a millimeter, to permit of microscopic observation. Assume first that the cell is closed on all sides and filled with the suspension free of air bubbles. Then consider that the surface of the cell wall toward the water is the seat of an electrical double layer. Usually the glass wall is negatively charged and the water positively; the negative charge is fixed on the glass, while the positive layer exists in the water and therefore is movable. If, now, an external electro-motive force is applied, the positive part of the double layer is moved tangentially, carrying the water with it; and as the result of friction the more remote water layers will also be carried along. Since, however, the water cannot flow out of the closed cell, motion in the reverse direction must occur in those "layers" of water most remote from the wall. The water thus will be dragged along in one direction at its surface—tangentially to the cell walls—and the central portion will flow back in the other. Considering the water to be made up of narrow layers parallel to the upper and lower walls of the cell, the uppermost and bottommost layer ("upper" and "lower" being considered in the microscopic sense) move at maximum velocity; in layers farther in, the velocity is less, and at a certain distance becomes equal to zero, while in the central layer the direction is reversed. The velocity of the water therefore is a function of the distance, V_z, of a given water layer from the cell wall. If the total thickness of the microscope cell is designated by D, the velocity by u, and the maximum velocity of the upper and lower layers by u_0, then, according to v. Smoluchowski,

$$u = u_0\left[1 - 6\left\{\frac{V_z}{D} - \left(\frac{V_z}{D}\right)^2\right\}\right]. \qquad (8)$$

From this it follows, for example, that at a certain depth Z_o

$$Z_o = D\left(\frac{1}{2} \pm \frac{1}{\sqrt{12}}\right),$$

that is, at depths approximately $\frac{1}{5}D$ and $\frac{4}{5}D$, the velocity is equal to zero.

The flowing water sweeps the suspended particles along with it, and there is observed under the microscope a velocity of the particles which is the resultant of the cataphoretic motion of the particles and of the motion of the water. Only in the two layers $\frac{1}{5}D$ and $\frac{4}{5}D$, which may easily be measured with a micrometer, is the observed velocity that of pure cataphoresis.

As far as I am aware, v. Smoluchowski has not published anywhere the derivation of this theory. It may be presented as follows. Let the cell have the length, H, the breadth, y, and the comparatively slight depth, D. Let the corresponding 3 dimensions of the cell be oriented in the direction of the rectangular coördinates, x, y, z. The electric force acts on the upper and lower walls of the cell which have an area each $X\alpha = y$. The total resultant force therefore is $2xy\sigma H$, where σ is the electric surface density of the double layer on the glass wall, and H is the strength of the external field. This force presses the water against the side walls of the cell and gives rise to an equal and opposite mechanical force which, on account of the rigidity of the cell wall, is distributed over its whole surface, yD. If we consider now a thin section of water of thickness, dz, parallel to the xy plane lying at a distance, z, from the upper surface, then there is exerted on it a pressure $= 2xy\sigma H \frac{dz}{D}$.

The motion of the section which this force tends to set up is checked by the friction which the upper and lower surfaces of the section encounter in contact with the adjacent water layers. The friction on the upper surface of the section is $xy\eta\frac{du}{dz}$, where u is the velocity at the distance, z, from the upper surface of the cell. The friction on the lower surface of the section is oppositely directed, and is equal to $xy\eta\frac{du'}{dz}$ where η is the friction coefficient of water, and $u' = u + \frac{\partial u}{\partial z} . dz$. As total friction there remains the force,

$$xy\eta \frac{d^2u}{dz^2} . \mathrm{dz}.$$

At equilibrium, the force due to the electric field is equal to that of friction, hence,

$$\frac{2\sigma H}{D} = \eta \frac{d^2u}{dz^2}$$

or

$$\frac{d^2u}{dz^2} = \frac{2\sigma H}{\eta D}$$

By integrating twice we obtain,

$$u = \frac{\sigma H}{\eta} z^2 + c_1 z + c_2.$$

For $z = 0$, $u = u_0$, that is, the velocity of the upper layer $u_0 = c_2$. Again, for $u = u_0$ and $z = D$ we get $c_1 = -\frac{\sigma HD}{\eta}$, so that,

$$u = u_0 - \frac{\sigma HD}{\eta} z + \frac{\sigma H}{\eta} z^2. \qquad (1)$$

Now, since water as a whole does not undergo translation, $\int_0^D u dz = 0$. Whence, from (1),

$$\int u dz = u_0 z - \frac{\sigma HD}{2\eta} z^2 + \frac{\sigma H}{3\eta} z^3$$

and

$$\int_0^D u dz = u_0 D - \frac{\sigma HD^3}{2\eta} + \frac{\sigma HD^3}{3\eta} = 0$$

whence

$$u_0 = \frac{\sigma H}{6\eta} D^2. \qquad (2)$$

Substituting this in (1)

$$u = u_0 \left[1 - 6 \left(\frac{z}{D} - \frac{z^2}{D^2} \right) \right],$$ which is according to equation (8).

The theory of v. Smoluchowski is well confirmed by experiment. The microscopic technique of cataphoretic experiments in colloidal solutions was developed by Ellis [7] and by Powis [8] and was later improved, and extended to ultramicroscopic observations by Svedberg and Andersson.[9] Ellis and Powis studied the motion of oil drops in water which was placed between slide and cover glass. Svedberg and Andersson avoided in two ways the disturbance caused by polarization at the electrodes. They either permitted the current to act only momentarily or else worked with alternating current, after Cotton and Mouton [10] had shown that cataphoretic motion follows readily alternations exceeding 1000 per second. The colloid particles were followed with the aid of the paraboloid condenser, and were registered photographically; the diffraction images of the particles generate lines of light the length of which may be accurately measured. The depth of their cell was 50-70 μ. Putter [11] could confirm v. Smoluchowski's theory approximately at least for bacteriological suspensions, although he worked under the cover glass with an incompletely closed cell. It is fair to assume that in such a case the water moved by cataphoresis does not run out of the cell and spread over the slide, but, in consequence of the incomplete wetting of the edge by the drop, instead of spreading out, it rather flows back in agreement with v. Smoluchowski in a closed cell.

It follows apparently from v. Smoluchowski's theory that the law implied in formula (8) is independent of the absolute depth of the cell. Therefore the water current in the middle layer of the cell must in all cases possess half the velocity (in the opposite direction) of that at the rim. This does not hold, however, in the case of *macroscopic* cataphoresis experiments in U-tubes. Hence, first, this law holds only for very narrow cells in which laminar motion, only, of the water occurs, and secondly, in a U tube the upward motion along the walls raises the edge of the upper meniscus merely far enough for the hydrostatic pressure to counteract the movement, after which motion of the water ceases and pure cataphoresis is observed.

4. Streaming Potential

If a liquid is forced through a porous membrane or through a capillary, a potential difference—called *streaming potential*—is set up between the two ends of the capillary. If, by means of metal electrodes, this potential is allowed to act on a closed circuit a so-called *streaming current* will flow. This phenomenon was described by Quincke.[12] A clay plate was inserted between the ground ends of two glass tubes, or a powder was tamped into a glass tube to form a diaphragm. Water was then forced through the tube under pressure and the potential tapped off by means of platinum electrodes inserted at either side of the diaphragm. The electromotive force due to the flow was proportional to the net hydrostatic head, regardless of the thickness or manner of constructing the diaphragm, so long as the latter was of the same material chemically. The phenomenon was described later by Zoellner,[13] Edlund,[14] Haga,[15] and Clark.[16] The explanation of the phenomenon is as follows: The movable portion of the electrical double layer is carried along by the water current, whereby the upper end of the capillary picks up a free charge with respect to the adhering layer, and the liquid below the lower end of the capillary acquires an opposite charge with respect to the movable portion of the double layer. The value, E, of the streaming potential according to Helmholtz, is given by the formula:

$$E = \frac{\zeta P D}{4\pi\eta\lambda}$$

in which ζ is the potential of the double layer, P the net head, D the dielectric constant of the liquid, η the friction coefficient of the latter, and λ its specific conductance. The factor, 4π, is introduced to reduce to electrostatic units; if ζ and E are expressed in volts, it is necessary, once more, to multiply by 90,000. The electro-motive force of the streaming current is thus proportional to the hydrostatic head, and to the ζ-potential, being inversely proportional to the internal friction of the liquid and to its conductivity. The last is particularly noteworthy; it is because of this that satisfactorily measurable streaming potentials are obtained only by employing solutions in which the electrolyte concentration is very low. Even in the case of electro-endosmosis the transfer of water diminishes, in general, with increase in electrolyte concentration; from which it may be concluded that ζ diminishes in the presence of much electrolyte. Therefore the streaming potential also diminishes with increasing electrolyte concentration; but this diminution is very much greater than the endosmosis, since the increased conductivity also reduces the streaming potential very greatly. Whereas for endosmosis experiments good results are obtainable sometimes with 0.1 molar and stronger salt solutions, it is necessary in the case of streaming potential experiments to work with concentrations of the order of 10^{-6} normal.

The converse of streaming potential will be merely mentioned in passing: if fine particles (say, silver powder) fall through a cylinder filled with water, a potential difference is set up between the ends of the cylinder.[17] (See paper by E. F. Burton, this volume. J. A.)

5. Application of the Theory of the ζ-Potential to Colloid Solutions

In general, a potential difference evidently arises at any phase boundary whatsoever. The classification into electro-endosmosis, cataphoresis, and streaming potential is simply a device to assist in its confirmation and measurement. It may be assumed therefore that in general a potential difference exists at the boundary between any dispersed phase and the dispersing medium, and the question arises as to what effect this potential has, especially whether it is of any significance regarding the state of the colloid. To anticipate the answer, it has been shown that this potential is one of the most important factors in the determination of the colloidal state. To be sure, it is impossible to state in advance, for example, what degree of dispersion, what viscosity, etc., any colloidal solution whatever possesses for a given potential difference; that, rather, is characteristic of the individual colloid. Thus, gelatin, for instance, forms a stable colloidal solution even in the absence of any potential, while mastic does so only under conditions which permit the maintenance of a potential of several centivolts. However, for a given colloid the properties depend in a clearly evident manner upon the potential. The case is similar to the contact potential between a metal and a solution, which, first of all, is determined by the specific nature of the metal. For a given metal, however, the potential varies according to the Nernst logarithmic concentration rule. Similarly for every colloid there exists an individual property, not readily predictable, and upon this the influence of the boundary potential always is superposed. This influence in general is such that the stability of the solution increases with an algebraic increase in the interfacial potential. In the case of reversible, spontaneously dispersing colloids (albuminous bodies), the dispersion is increased with rise in potential; turbid solutions become clear; the Tyndall effect becomes weaker; and so on. With a non-spontaneously dispersing colloid (such as gold, mastic, etc.), appropriate reduction of the potential induces direct flocculation. In this case, accordingly, we may say directly that the interfacial potential is essential to stability. Indeed, such colloidal solutions can *form,** moreover, only if through some process (reduction of gold chloride; water addition in the case of the alcoholic mastic solution) the micells of the colloid *come into existence* under such circumstances that a sufficient interfacial potential is established throughout the whole process.

The action of the electrical double layer consists simply in hindering the approach of the micells to such proximity that the cohesion forces can act. The outer layers, with their similar charges, act like mechanical buffers; in order that the particles may touch one another the repulsion of the approaching outer layers must be overcome, the outer layers must be broken through. The possibility of this occurrence is reduced by increasing the charge of the double layer. On the other hand, it is conceivable that this charge need not be equal to zero in order to permit flocculation. The repulsion between two micells is not like that between two spheres carrying *free* electric charges. Considered from afar, a micell with its double layer is electrically neutral; only on close approach of two micells does the space distribution of the double layer bring about a preponderance of repulsion over attraction. The repulsion of two particles decreases in proportion to the distance to a very high power. In very concentrated mastic solutions Perrin was, in fact, able to detect a repulsion, in that the particles were not distributed in size according to the simple hypsometric formula; their osmotic pressure, therefore, is greater than it would be according to Van't Hoff, employing the Avogadro number.

So much for the physical phenomena of endosmosis and cataphoresis;

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* This means, can exist for a measurable period. J. A.

there follows a consideration of the influence on potential, of the *chemical* nature of the dispersed substance.

6. Perrin's Investigations

Perrin[18] carried out his investigations with an apparatus of the type shown in the subjoined sketch (Fig. 1). The diaphragm is represented by the glass tube, *M*, which is filled with the pulverized material. *A* and *B* are the electrodes. The movement of the water is observed through the change in level of the water column in the nearly horizontal, sloping tube, *G*. The electric field as a rule was such that between the electrodes the potential gradient was about 10 volts per cm. Perrin found almost immediately that only markedly ionizing liquids show strong electro-osmosis. Liquids of small dielectric constant, which themselves are poor conductors and cause only slight dissociation of dissolved electrolytes, show little or no electro-osmosis. Chloroform, petroleum ether, benzol, turpentine, CS_2, showed absolutely none. Of the opposite type were nitrobenzol, acetone, ethyl alcohol, methyl alcohol, and especially water.

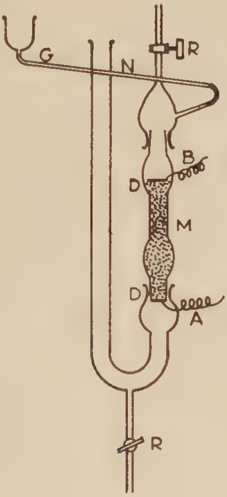

Fig. 1.

The particular electrolytes dissolved in the water have a marked influence on the magnitude and direction of endosmosis. Acids and alkalies, in other words, H and OH ions, have an exceptionally strong influence. Perrin found a whole series of powders in which the direction of endosmosis in weakly acidulated water was opposite from that in faintly alkaline water. In acid solutions the water always migrated toward the cathode; that is to say the powder was charged positively with respect to the acid solution and negatively with respect to the alkaline. Such substances as carbon, sulfur, carborundum, naphthalene, salol, $CrCl_3$, AgCl, $BaSO_4$, ZnO, CuO, gelatin, etc., were tried. The Table I on page 482 gives the magnitude of the results in ccm. water per minute for a few substances, employing a diaphragm cross-section of 1.4 cm.

TABLE I

Diaphragm Material	Nature and Molal Concentration of Solution	Charge on Wall	Volume of Water Transferred, C.C./Minute
Al_2O_3	$1/500$ HNO_3	+	110
	$1/2500$ HCl	+	70
	$1/500$ NaOH	—	55
	$1/250$ NaOH	—	90
$C_{10}H_4$ (Naphthalene)	$1/50$ HCl	+	38
	$1/100$ HCl	+	39
	$1/1000$ HCl	+	28
	$1/5000$ HCl	+	3
	$1/5000$ KOH	—	29
	$1/1000$ KOH	—	60
	$1/50$ KOH	—	60
$CrCl_3$	$1/1000$ HCl (or HBr, HNO_3 or HAc)	+	95
	$1/500$ KOH (or LiOH, etc.)	—	85
AgCl	$1/500$ HCl	+	30
	$1/500$ KOH	—	50
$BaSO_4$	$1/500$ HCl	+	9
	$1/250$ KOH	—	7
H_3BO_3 (Boric acid)	Saturated soln. acidified with HCl	+	2
	Saturated soln. without addition	—	10
Sulfur	$1/50$ HCl	+	22
	$1/500$ HCl	?	0
	$1/500$ KOH	—	65
	$1/50$ KOH	—	92
Salol	$1/50$ HCl	+	18
	$1/500$ HCl	?	0
	$1/4000$ HCl	—	10
	$1/4000$ KOH	—	50
	$1/50$ KOH	—	65
Carborundum	$1/50$ HCl	+	10
	$1/125$ HCl	?	0
	$1/500$ HCl	—	15
	Distilled water	—	50
	$1/5000$ KOH	—	60
	$1/500$ KOH	—	105
Gelatin	$1/50$ HCl	+	22
	$1/100$ KOH	—	35
Cellulose	$1/50$ HCl	?	0
	$1/500$ HCl	—	20
	$1/500$ KOH	—	70

From this table it may be seen that the substances investigated have a positive charge in acid solution and negative in alkaline solution. The point of reversal, however, is not in every case the neutral solution. Perrin believed that the cause of this lay in secondary disturbances, for example, partial dissolution of the powder and consequent change in the acidity, or the presence of polyvalent ions which, as has been seen, have a great influence on these phenomena. He derived the following rule:

Every non-metallic substance (in the absence of polyvalent ions) is positive in an acid solution and negative in an alkaline solution.

As a matter of fact he himself noticed that the point of reversal of the electric charge does not always lie exactly at the point of chemical neutrality.

Table I shows this in a striking manner for cellulose. With this material, as with iodoform, no positive charge was set up even in $\frac{1}{50}$ N HCl. Accurate insight into these relationships evidently involves the same considerations as the theory of the isoelectric point for dissolved ampholytes, which had not been developed at the time Perrin made his investigations. Perrin realized, however, with his characteristic farsightedness, that the above rule was approximate only, and set up the following as holding rigidly:

The electric potential between any sort of wall and a solution, is always increased on the addition of a (univalent) acid and always diminished on the addition of a (univalent) base.

7. THE ISOELECTRIC POINT OF DIAPHRAGMS; DIAPHRAGMS WITH AND WITHOUT ISOELECTRIC POINT

Further experiments by Bethe and Toropoff,[19] by Glixelli,[20] and by Gyemant,[21] with a somewhat different technique which permitted the accurate maintenance of the p_H at the electrodes, showed that in general it is incorrect in principle to look for the reversal at the neutral point. To be sure, the two agree in the case of blood charcoal, gelatin, and a few other substances. Nevertheless there is a whole series of substances which, however strongly acid the reaction, display no positive charge, but at most a neutralization of the previously existing negative charge,—for example, cellulose, collodion, agar, kaolin; retort carbon, also, belongs in this class according to Bethe and Toropoff; gelatin, however (*i.e.*, gelatin-impregnated collodion membranes of the type devised by Jacques Loeb [22] or membranes of chilled gelatin), does not show reversal at the neutral point, but rather at that H-ion concentration which I [23] had found to be the isoelectric point by means of cataphoresis experiments with dissolved gelatin.

Table II, below, gives a few of the results obtained by Glixelli.[24] He found first a few diaphragm materials which, like the majority of Perrin's materials, showed a reversal of charge on going from acid to base; it is very significant, however, that the reversal in most cases does *not* occur at the exact neutral point.

TABLE II

	v Endosmosis Velocity
BeO	
Distilled water	−1.59
0.0001 N NaOH	−0.87
0.00016 N NaOH	+0.21
0.001 N NaOH	+1.84
ZnO	
Distilled water	−0.31
0.0002 N NaOH	−0.22
0.0003 N NaOH	+0.16
0.0004 N NaOH	+0.24
$Mg(OH)_2$	
0.0006 N NaOH	−0.64
0.01 N NaOH	−0.05
0.02 N NaOH	+0.90

Isoelectric point for a given *h* (mostly in alkaline solution).

	Endosmosis Velocity
Silicic Acid ($SiO_2 . nH_2O$)	
Distilled water	+0.63
0.03 N HNO_3	+0.33
0.05 N HCl	+0.30
0.47 N HNO_3	+0.12
Antimony pentoxide (Sb_2O_5)	
Distilled water	+1.27
0.076 N HCl	+1.27
0.63 N HCl	+1.08
Tungstic acid (H_2WO_4)	
Distilled water	+2.66
0.045 N HCl	+1.12
0.207 N HCl	+0.28
0.8 N HCl	0.00

Still no reversal in extremely high acid concentration.

The experiments which Gyemant [25] carried out in my laboratory yielded the data of Table III.

TABLE III

Membrane	Electrolyte Solution	Charge on Membrane		Relative Velocity of Endosmosis	Remarks
Collodion	Distilled water	—		16.0	Always negative, even in HCl and $AlCl_3$; almost discharged by the last two, however.
	0.01 N HCl..........	—		11.0	
	0.001 N NaOH	—		15.2	
	0.001 N NaCl	—		12.4	
	0.001 M $CaCl_2$	—		8.8	
	0.001 M $AlCl_3$	—		1.0	
	0.001 M Na_2SO_4	—		18.1	
Kaolin	Distilled water	—		38.0	Almost always negative; in very conc. HCl completely discharged; positively charged only in $AlCl_3$.
	0.001 N HCl	—		61.7	
	0.01 N HCl	—		6.5	
	0.1 N HCl	0		0.0	
	0.001 N NaOH	—		182.5	
	0.001 N NaCl	—		259.0	
	0.001 M $CaCl_2$	—		145.8	
	0.001 M Na_2SO_4	—		288.8	
	0.001 M $AlCl_3$	+		202.7	
Blood Charcoal	0.001 N NaCl	—	pH according to adsorption	12.8	Isoelectric point at pH = 4. Salts give sometimes +, sometimes — charge.
	0.001 M Na_2SO_4	—		46.0	
	0.001 M $AlCl_3$	+		39.5	
	0.0025 N HCl	—	4.35	4.2	
	0.0005 N HCl	+	3.95	7.0	
	0.001 N HCl	+	3.78	14.0	
	0.01 N HCl	+	2.00	26.0	
	0.002 N $AgNO_3$	+	—	10.2	
2 Per Cent Agar Jelly	0.001 N NaCl:				Always negative as in case of collodion, even with $AlCl_3$.
	Membrane 1 cm. thick	—		70.0	
	“ 2 “ “	—		69.0	
	“ 3 “ “ *	—		78.0	
	0.002 M $AlCl_3$.......	—		13.0	
	0.001 N HCl........	—		54.0	
Fe_2O_3	Water	+		10.5	Isoelectric point at faintly alkaline reaction; negative only in OH ions.
	0.001 N HCl	+		67.0	
	0.001 N NaOH	—		16.0	
	0.001 N NaCl or RbCl	+		23.0	
	0.001 M $CaCl_2$ or $BaCl_2$	+		62.0	
	0.001 M $AlCl_3$.......	+		103.0	

* Since in the experimental arrangement of Gyemant the thickness of the membrane forms only a small part of the path between the electrodes, the current strength will not be affected appreciably by variations in its thickness. Under these conditions endosmosis should be independent of the thickness of the membrane as is confirmed by experiment.

8. THE SIGNIFICANCE OF POTENTIAL

From the facts established regarding the influence of electrolytes in solution, it follows beyond a doubt that it is ions and not free electrons which form the basis of the electrical double layer. It is conceivable either that the molecules in the surface layer of the electrically neutral micells have a tendency to dissociate electrolytically in such a way that they tend to send out one ion species as the movable component of the double layer, while the associated, oppositely charged ion species remain attached to the micell, or, as it may also be put, adsorbed; or that one of the ion-species in the solution is adsorbed by the electrically neutral micells, whereupon it follows from the principle of electrostatic attraction that a group of oppositely charged ions is accumulated in the adjacent layer. Finally there is another case in which the micell itself is not, or at least not appreciably, active in building up the double layer, and the double layer arises from the fact that the ions in solution arrange themselves in a double layer at the boundary as a result of *internal* forces. If we simply carry the adsorption idea far enough, we can explain the phenomena by stating that one ion species is adsorbed at the interface more strongly than the other. Thus if we have adopted a purely formal and most far-reaching definition of adsorption, we may consider the origin of every double layer to be due to adsorption phenomena. This definition must run as follows: by adsorption we understand the phenomenon that a molecular species in a solution attains a higher concentration at the surface of this solution or at the interface adjacent to another phase, than in the body of the solution. This definition of course is purely formal and leaves open the question whether the process is brought about by chemical or by physical forces, and whether the second phase exerts an attractive force on the adsorbed molecular species, or whether the whole phenomenon rests upon forces which act solely within one phase. At first we shall employ the idea of adsorption only in this broadest sense. In our case the molecule to be adsorbed must likewise be always an *ion* species, otherwise its adsorption could not give rise to a difference in potential between the boundary and the internal solution. Since, according to the principle of Gibbs surface active substances tend to concentrate at the free surface of the liquid, the case is also conceivable in which the free surface of a liquid is richer in one ion species than another. In this case the vapor space which, in comparison with a liquid is practically without mass, is in a certain sense the "adsorbent." This is, of course, a purely formal definition, but it has the advantage that it permits the consideration, from the standpoint of a common property, of all those "ion distributions" at the interface which give rise to a potential difference. If it becomes a question of distinguishing between the latter form of adsorption and the particular adsorption by the surface layer of a second massive phase, I would suggest that the adsorption of empty space be called "apparent" adsorption as distinguished from true adsorption. With ion adsorption different cases are possible; one corresponds more to the chemical, the other to the so-called physical adsorption. This depends, namely, on whether the adsorption is electro-polar in character or not. We distinguish, therefore, *apolar* and *polar* adsorption.

Of *apolar* adsorption, the best, in fact the only certain, example, is adsorption at the surface of carbon, preferably *blood* charcoal. Although this material is not obtainable entirely free from contamination by polar substances (Ca-salts, and the like), nevertheless, as I have pointed out, the polar part of the adsorption, due to the impurities, is readily distinguished from the apolar; furthermore, the apolar part is very slight (a few per cent) when dealing with the adsorption of electrolytes. Apolar adsorption is recognizable by the fact that equivalent quantities of the cations and anions of the electrolyte under examination are always adsorbed, which is far from being the fact in polar adsorption. Thus, for example, in the case of the adsorption of methylene blue chloride by carbon, so far as chemical analysis permits it to be determined, just as much color base as chlorine is adsorbed; according to the law of electrical neutrality there is no other possibility. (At most, were it conceivable that OH is adsorbed instead of Cl, this would signify hydrolysis of the salt as the result of adsorption. This is not determinable with certainty in the case of carbon.) Since, however, the adsorptive forces on these two ion species are unequal, the more weakly adsorbed ion species group themselves as the outer component (projecting into the liquid), while the more strongly adsorbed species form the inner (attached to the carbon) component of the double layer. The charge on the carbon therefore is always that of the more strongly adsorbed ion species. Now endosmosis experiments with carbon as the filtering medium give us the charge on the carbon. They have shown, for example—if we may accept as correct the significance, just stated, of these experiments—that the H-ion is more strongly adsorbed than most other cations; that is, carbon adsorbs an acid more strongly than it does the salts of the same acid. In the second place, the H-ion is also more strongly adsorbed than most anions. These statements have their basis in the observation that, first, a (strong) acid is in general more strongly adsorbed than its salts; secondly, blood charcoal is found from electroendosmosis to be positive, with respect to the solution, in solutions of strong acids. Only in a few organic acids is blood charcoal negative, and these acids are further distinguished by being appreciably more strongly adsorbed than the simple inorganic acids. The following is in good agreement basically with the foregoing theory: An acid of which the anion is so strongly adsorbed that it even charges the carbon negatively in spite of the presence of the H-ion, must be much more strongly adsorbed on the whole than ordinary inorganic acids in which the anion resists adsorption and remains in the outer component of the double layer. Further, OH ions are more strongly adsorbed than most anions; that is, NaOH is adsorbed more strongly than NaCl, NaBr, etc., and carbon is negatively charged in NaOH.

Since writing the above, very active carbon, entirely free from ash content, has been prepared by the heat activation process (Miller[37]; Ogawa[38]). This carbon has somewhat different properties, in that it is not positively charged by acids, and adsorbs NaOH less than it does HCl. The carbon obtained by cokeing pure organic substances resembles generally the blood charcoal described above, and acquires the properties of "activated" carbon in proportion as it is strongly heated. There is nothing characteristic about the ultimate analysis of the various kinds of carbon, *e.g.*, from cane sugar; there is probably involved a structural change, the crystal structure of graphite coming more and more into evidence upon heating. These new investigations do not materially affect the general view given above.

Under *polar* adsorption, numerous adsorbing media are available for consideration; we shall confine ourselves to two types: (1) the silicates (kaolin, kieselguhr, etc.), and (2) a few metal hydroxides (iron and aluminium hydroxides). The conceptions which have gradually been built up concerning the mechanism of amorphous adsorbents I have summarized as follows: Take, say, amorphous calcium silicate; this salt, like all salts, has the tendency to ionize and thus form Ca and silicate ions. However, silicate ions do not appear to be capable of individual existence; there is no definite, molecularly dispersed and totally dissociated stable solution of any sort of silicate. The silicate ions do not appear to be in the form of single, independent ions, but remain in association. The electrolytic dissociation of an ordinary salt in a medium of sufficiently high dielectric constant (like water) rests on the fact that in this medium the attraction of the oppositely charged ions is so weakened, that the water can force itself between the ions; the electrostatic attraction of the individual ions by the (likewise polar) H_2O molecules, is greater than by the oppositely charged ion. Now, as is known, the free, surplus charge on an ion is not the only charge; there are others which are compensated by equal opposite charges. Thus there are individual regions of positive and negative charge in every molecule.* Silicic acid ions exert on one another such strong electrostatic attraction, that the H_2O molecules cannot force themselves in between. The electrolytic dissociation of calcium silicate consists, therefore, in the production of free, independent Ca ions, the silicate ions, however, grouping themselves together and remaining bound with the amorphous aggregations to which they belong. Consequently, under the circumstances, only a surface layer of this aggregation has the possibility of throwing off Ca ions, and these must remain in the vicinity of the outer component of a double layer. Such ions as silicic acid may be called "colloidal ions" or "lazy ions." † The case is similar with iron and other hydroxides. These always contain other ions. If, for example, $Fe(OH)_3$ is prepared by precipitating $FeCl_3$ with NH_3, the Cl is found indissolubly bound up with the precipitate. A complex Fe — OH — Cl compound must be assumed, regarding the exact composition of which one can only hazard a guess.[26] This splits off OH or Cl ions, but develops a colloidal, Fe — containing cation which cannot go into solution. In the case of the silicate, the anion, accordingly, is the "lazy," colloidal ion, while in the case of iron hydroxide the cation is colloidal. The electrical phenomena are in complete agreement with the above. The colloidal ion may be either an anion or a cation; furthermore it is to be expected that like other ions (albumin, amino-acids), colloidal ions may also be positive or negative, depending upon external conditions, especially the p_H value of the solution. Experience has shown that there are countless amorphous substances which form a negative colloid under all conditions; for example, silicates of the most varied composition, the resins, the higher fatty acids, etc. Furthermore, there are numerous amphoteric colloidal ions; albuminous substances (albumin, glue, silk, wool, metal hydroxides like those of Fe or Al); their charge depends to a particularly large extent on the p_H. The isoelectric point lies at a certain p_H; this occurs either on the acid side as is true of the majority of albuminous bodies, or on the alkaline side (many metal hydroxides). On the other hand, no amorphous substance has been discovered up to the present time which, while retaining its property of being molecularly dispersed and insoluble, yet forms positive colloidal ions under all conditions. Non-amphoteric metal oxides such as, for instance, AgO, Na_2O, etc., always dissolve in the *ionized* form, so that colloidal ions do not get a chance to form.

A factor common to all of these cases is, that there are no *independent* ions of the substances, except the colloidal ions. Thus silicates or silicic acids in general are only colloidally soluble. Likewise it has not been possible to show that a suspension or a colloidal solution of $Fe(OH)_3$ contains that complex, Fe — containing ion also in the ionized form. Of these cases certain ones are to be distinguished which the colloid-forming element, or adsorbent, possesses in addition to a well-defined although small solubility. Thus, for example, AgI possesses a very slight solubility, but it is perfectly definite owing to the constancy of the solubility product, $[Ag] \cdot [I]$. A suspension or colloidal solution of AgI therefore always represents, in addition to the suspended particles of AgI, some independent Ag and I ions in solution, and neither Ag nor I has the properties of a lazy or colloidal ion. The possibility of a suspension of AgI exists only when more AgI is present than is capable of dissolving. Also, such an undissolved particle of AgI will, in general, be endowed with an electrical double layer; if AgI is precipitated out of $AgNO_3$ by adding excess KI, then the AgI will be negative, as Lottermoser[27] has shown.* If excess $AgNO_3$ is used, then the precipitated AgI is positive. Evidently I ions are adsorbed in the former case, Ag ions in the latter. This sort of adsorption may be elucidated most clearly through a conception developed by Haber.[28] In the AgI crystal there is a cubical arrangement of the Ag and I ions; each valence of an I ion is broken up into six components and unites with each valence component of an Ag ion. Consequently free valence bonds must exist at the surface layer of atoms of the crystal, at the I ions as well as the Ag ions; these valence bonds tie together oppositely charged ions. Thus each surface of a crystal, and moreover apparently every surface of any sort, possesses adsorptive power for ions. Depending on the concentration of the Ag and I ions in solution, the adsorption of Ag or of I ions will predominate, and the particle take on a positive or a negative charge.

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* See paper by I. Langmuir, this volume. J. A.

† McBain speaks of colloidal electrolytes. J. A.

Further discussion of this question, especially as it relates to whether the earlier view and that of Haber are merely different presentations of the same underlying facts, belongs rather more fittingly in a chapter on adsorption than in one on electrical phenomena. For the present purpose it will suffice to be able to derive a picture of the mechanism of the electrical double layer, sometimes in one way, sometimes in another, consistent with the conceptions of atomic physics. All of these conceptions, however, have been, thus far, of a qualitative nature only. We shall endeavor now to present what little is known of the quantitative relationships. In the first place it should be pointed out that a definite and intimate relationship does not exist.

9. The Invalidity of the Nernst Potential Formula

Following out the conception developed above, we may consider a mastic particle in a colloidal mastic solution, as being classed as an "electrode" in the sense that it, like a hydrogen electrode, has a tendency to send H ions into solution. Consequently one might conjecture that the potential, π, of a mastic particle might be expressed from p_H of the solution according to the Nernst formula,

$$\pi = \frac{RT}{n} \, ln[H^+]^+ \text{const.}$$

Experience has shown,[29] however, that this relationship does *not* hold, if by the potential of the mastic particle we understand that potential which may be calculated on the basis of electric cataphoresis. Numerous experiments in the literature form the basis for this conclusion, and I have convinced myself of it, especially for mastic, by careful experiments (with Domboviceanu), not previously published. It is true qualitatively, to be sure, that the negative potential of the mastic becomes increasingly smaller (negative) with increasing H concentration and finally reaches zero; however, the variation is less in proportion than would be anticipated on the basis of the Nernst formula. According to the latter, a potential of 58 millivolts corresponds to a tenfold change in H concentration; actually the potential difference is much smaller, usually less than 10, and in certain cases only 5 to 6 m. v. Furthermore, it has not been possible to show, as required by the Nernst formula, that the charge is reversed at very high H-concentration. One might try to explain this discrepancy in the following manner. The Nernst formula rests on the assumption that the electrode is in chemical equilibrium with the solution. For this reason it is not applicable, for example, to the case of a zinc electrode dipping in a solution which contains, say, Cu ions in addition to Zn ions. Similarly, mastic is not in equilibrium with a given electrolyte solution, because experience shows for example that mastic in a solution containing Ca adsorbs Ca, that is, H ions are exchanged for Ca ions. It is necessary, in order to exclude such a possibility, merely to carry out the cataphoresis experiments in HCl solutions of various concentrations. This is impossible practically, however, because HCl solutions dilute enough to render the mastic stable do not have sufficiently definite H^+ concentration. It is necessary to work with buffers; as such I chose an acetate, namely, the lowest possible concentration of sodium acetate $(\frac{1}{100}n)$. Here conditions are very favorable, for it scarcely is to be assumed that in the double layer Na ions are exchanged for H ions. In spite of this it was shown that the Nernst law again was not approached. Therefore there is some sort of error in this idea. In fact, I believe there are two sources of error. The first consists of the following essential difference between a metallic hydrogen electrode and a colloidal acid. The metallic electrode has the tendency at first to send H ions into solution and therefore to remain negatively charged; next, however, the opposite tendency ensues, H ions attaching themselves to the surface, which thereby becomes positively charged. The osmotic pressure of the H ions in the solution, determines which of these two tendencies predominates, and whether the electrode is positively or negatively charged. A colloidal acid, on the other hand, has a tendency to send H ions into solution and to remain negative; the reverse of which is merely the tendency again to take up these H ions which have been split off and completely discharge itself. On the contrary, we cannot ascribe to a colloidal acid the tendency to take up H ions from the solution and become positively charged. Such a substance could no longer be referred to as an acid. Accordingly it is not to be expected that by varying the H ion concentration of the solution, the charge can pass the null point, which is characteristic of the theory of the Nernst electrode. Even on these grounds the charge on a colloidal acid cannot possibly vary with the H ion concentration according to the Nernst logarithmic law. The second consideration lies in the fact that it is exceedingly questionable whether a potential which can be calculated for the boundary between two phases from any sort of thermodynamic considerations, is identical with that potential which appears as the measure of cataphoresis in the Helmholtz formula. The potential at the boundary of a colloidal micell may be calculated, however, simply from the velocity of cataphoresis or related phenomena by means of the Helmholtz formula. The reason why the potential calculated according to Helmholtz cannot possibly be identified directly with a potential difference between two phases derived from thermodynamic considerations, becomes quite clear if we undertake a revision of the theory of Helmholtz, which was propounded in advance of the ionic theory, and take into account more fully the properties of ions, the material substrate of the double layer.

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* See paper by A. Lottermoser, this volume. J. A.

10. Gouy's Theory

It will be best to begin with a presentation of the ideas of Gouy[30] and Chapman.[26]

The Helmholtz conception of the electrical double layer is two free electric charges spread out *flat* as in a condenser; the idea of the *flat* distribution of the double layer is attributed also to the Nernst theory of the electrode double layer. However, it is without significance for the Nernst potential whether or not this conception proves correct, but as soon as we consider electro-kinetic phenomena, an accurate conception of the intimate structure of the double layer becomes of great significance. Now Gouy has developed the view that at least the component of the double layer which belongs to the free liquid, not only has a flat structure but also possesses depth; this property of the double layer he called its "diffuseness." The free ions which make up this component of the double layer do not lie in a strictly flat plane; instead the situation is to be visualized as follows: in the liquid adjacent to the solid boundary there are the same positive and negative ion species as within the liquid; and it is only the *concentration,*—whether there are one or more positive or one or more negative ion species,—that is greater in the vicinity of the boundary than within the liquid. The charging ions of the double layer are not the individual ion species present in the boundary layer, but rather they are the positive (*or* negative) charge due to the ions which exceed neutrality. Accordingly, then, there is merely an enrichment, in the boundary layer, of cations and a depletion of anions (or the reverse). Gouy[30] therefore postulated that an ion species in the liquid is electrostatically attracted by the charged wall (or as the case may be, repelled), while on the other hand osmotic forces have a tendency to equalize the ion concentration everywhere. For certain simple conditions, Gouy developed a quantitative relationship. Let N_K and N_A be the concentrations of the cations and anions, respectively, within the body of the solution; and assume that only these two ion species are present. Further, let A_K and A_A be the coefficients by which N_K and N_A must be multiplied in order to give the concentrations of the ions in the surface layer; the first of these factors is >1, the other <1, and these factors vary, with the distance, z, from the solid wall in such a manner that both approach the value 1, for a great distance; corresponding to the distance, z, from the surface, let c be the free electric charge per *unit surface,* and D the dielectric constant. Then, according to Gouy,

$$N_K(A_K - 1) + N_A(A_A - 1) = \frac{2\pi e^2}{DRT}$$

According to the explanation given above either $(A_K - 1)$ *or* $(A_A - 1)$ is always negative. The resultant electric effect of this diffuse double layer may be considered to be *replaced* by a *surface layer* of free electricity if the latter is given a certain location, namely, if it is transferred to the center of gravity of the diffusion layer. One may also consider the diffuse electric layer to be replaced by a Helmholtz flat surface layer of a given thickness, δ, although this thickness varies over a wide range. The more diffuse the double layer, the larger must this value, δ, be assumed to be.

The greater the charge and the more concentrated the ions in the solution, the less will be the "diffuseness" of the double layer and the smaller, therefore, the fictive value of δ. Gouy calculates for a charge at the boundary of 10 electric units that $\delta =$ in 0.1 n solution $= 0.00096\mu$, in 0.001 n solution $=$ $0.0096\ \mu$, in theoretically pure water $= 0.01\ \mu$.

For large charges and for concentrated solutions, δ becomes so small that we practically can make use of the conceptions of the Helmholtz theory, viz., two electric *layers* opposite each other in a certain spacing; in solutions deficient in ions, however, the diffuse layer extends noticeably into the solution.

Recently O. Stern [29] has advanced a theory of the diffuse double layer, which is probably nearer the truth than that of Gouy.

11. The Difference Between ζ and ε

The conception of a surface-like double layer consequently may be considered as only a useful substitute, in certain instances, for the actual conditions. At least the outer component of this double layer is not exactly a layer but a physical structure of appreciable depth. If we imagine the latter to be cut up into laminations parallel to the solid boundary, these will not have equal potential, but the latter will vary with the distance. The "Potentialsprung" of Helmholtz between points within the liquid is transformed into a gradual change. This view was first clearly developed by v. Smoluchowski,[31] and especially by Freundlich.[28] In the accompanying sketch (Fig. 2), *AC* represents the boundary between the solid body, *S*, and the liquid, *L*. Then the variation of the potential according to Helmholtz is indicated, for example, by the broken line, *EBCD*, where the ordinates represent potential and the abscissæ the distance from the boundary. *A* is the origin of abscissæ. According to Smoluchowski the actual course is depicted by the curve, *ED*. If now we consider an electric force acting as the result of an externally applied potential drop tangential to the interface, the latter will act on the flat—say the negative—segment of the solid wall in the opposite direction from that on the free positive charge of the liquid. The free ions must drag the water along in some manner. Now the water adheres to the wall and the external electric force can set in motion only those water laminæ whose adhesion to the wall it may overcome. In cataphoresis and endosmosis the water laminæ next to the solid wall do not move (just as in the flow of water through a capillary, the water film adjacent to the wall flows practically not at all) but one water lamina moves against another relatively fixed *water lamina*. The water lamina fixed by the wall is the lamina between *A* and *F*. The potential difference which is calculable from cataphoretic velocity by means of the Helmholtz formula, is that between the two layers moving relatively to each other. For the Nernst potential, ε, there is to be considered only the algebraic sum of the work which must be expended when an electric point charge is moved from a point within one phase to a point within the second phase; for this purpose it is immaterial whether the force (the potential difference) which accomplishes this work, actually lies at a point in the separating interface, or whether it is distributed to a certain extent on both sides of the interface; whether it is a question of a discontinuous jump in potential or a gradual change in potential

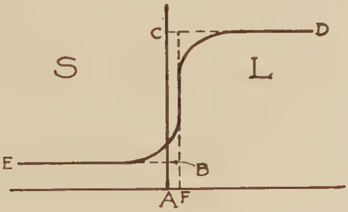

Fig. 2.

which may even rise and fall. For electro-kinetic phenomena, on the other hand, only that fractional part of the ε-potential is to be considered which prevails between the motionless water layer and that moving against it. In general, the ζ-potential will therefore have the same sign but a smaller magnitude than the ε-potential; the case may also arise in which the ζ-potential has the opposite sign to the ε-potential. Such cases have been pointed out by Freundlich and his co-workers. This case appears especially capable of occurring if the solution contains strongly adsorbable, tri-valent ions.

The Nernst ε-potential cannot be affected by adsorption phenomena at the interface; it is uniquely determined by the nature of the electrode and the concentration (preferably the activity) of that ion species which the electrode is capable of sending out; it is, however, independent of other ion species, or to put it in better form, it is dependent on other ion species only in so far as the latter influence the activity of the "characteristic" ion species. The ζ-potential, on the contrary, is dependent on the intimate structure of the layers in which the potential change lies.

12. COLLOIDS AS ELECTROLYTES

An individual micell of a colloidal solution, inclusive of its electrical double layer, behaves, under the influence of an electrical potential drop, in many respects similarly to the individual molecule of a dissolved electrolyte. In both cases there is, to begin with, a space separation between the moving positive and negative particles, which may be designated as *electric dissociation.* In the case of the truly dissolved electrolyte, this results in the splitting of the molecule into two individual ions; in the case of the colloidal micell it produces a splitting into the two sections of the double layer. In both cases the carriers of the opposite charges move in opposite directions under the influence of an external electric force. This motion is called conduction in the case of a pure electrolytic solution, and cataphoresis in the case of a colloid; both processes are completely analogous. In the case of the colloidal micells it is, so to speak, as though they consisted of independent, gigantic, polyvalent ions and equivalent quantities of ordinary independent ions of opposite charge. Between these two extremes lie all actual processes. The researches of McBain on soap solutions demonstrate the mechanism in a very instructive manner. The Na-salts of the lower fatty acids in water form pure binary electrolytes while those of the higher fatty acids assume more and more colloidal properties. Their anion component no longer exists as discrete fatty acid anions in solution, but form, instead, micells of fatty acids or of sodium salts of fatty acids, which are dissociated only at their surfaces. The circumstance of the anions remaining bound to one another brings about certain consequent electrostatic effects whereby the cations also, although perfectly free to move among themselves, are not distributed uniformly, but are arranged in the form of a diffuse layer surrounding the anion complexes, and appear in conjunction with the latter in the structure of the electrical double layer. In electrolytic conduction, the outer ions move in one direction the inner "giant" ion in the other. Since the latter also can retain within its interior Na ions, it follows that in this case part of the Na migrates toward the anode as McBain has shown. For this reason the relations become rather complicated, but on the whole the cataphoresis of soap particles appears to be simply the manifestation of the participation of colloidal particles in conduction, a conception first developed by v. Smoluchowski. Electrical conduction may be considered, from this, to be the limiting case of cataphoresis, when there is the greatest possible dispersion of the dissolved substance, when every individual electric charge is free to move independently of the others,—independently always insofar as the free mobility is no longer restrained by the ordinary adhesive forces between molecule and molecule, but only through the electric field which a single free charge sets up about itself, an effect which, in the earlier theories of electrolytic dissociation was especially neglected, and has only recently been applied to the theory of electrolytic dissociation as a result of the investigations of Herz, Millner, Bjerrum, Ghosh, and Boernstedt, and chiefly by Debye, and has furnished the basis of the theory of ion activities. While, however, this electrostatic effect is relatively slight in the case of pure electrolytes, so that for a decade it was overlooked entirely, and even today enters electrolytic dissociation calculations merely as a correction factor, its influence in colloidal electrolytes is so preponderating as entirely to dominate the phenomena. Here we no longer may speak of the independence of the ions of one another; the giant ions force a certain configuration on the free ions of the solution as well. It should be possible, now, so to shape the whole theory of electrolytic dissociation, that the conductivity of the ordinary electrolyte appears as the limiting case of electric cataphoresis. We still are quite remote from a solution of this problem. Helmholtz' theory of cataphoresis is based on the assumptions that the micells are relatively very large and that one may speak of a boundary surface of these micells in which a well defined electric density prevails. On the other hand, the electrolytic dissociation theory of Arrhenius presupposes that the electrolyte breaks up into independent ions with a simple or always limited number of elementary charges, and that the effect of the electric field which surrounds each ion, may be neglected in comparison with the mass effect that it would display in the unelectrified condition. A theory of electrolytic dissociation that embraces both cases has hitherto been entirely lacking; the experiments on which to build it are inadequate. I had attempted so to shape the theory as to treat the micells as an independent polyvalent ion and then to apply the law of mass action in the same sense that it may be applied, for example, to a polybasic acid. These theories, arisen before the appearance of Bjerrum's work, must today be considered to have failed on the grounds discussed above.* Recently Gyemant has conducted an investigation with the view to working out the dissociation of micells from the electrostatic point of view. But even with many simplifying assumptions, he was led to very complicated relationships, and the simplifying assumptions are made in such a fashion as to preclude the transition from the colloidal micell to an ordinary electrolyte. Accordingly up to the present it is possible merely to recognize qualitatively the similarity between a colloidal micell and a pure electrolyte, and to avoid entirely its quantitative expression. Indeed, the primary magnitudes which characterize the two cases are quite different. In a pure electrolyte we speak of concentration, degree of dissociation, dissociation constant. In referring to a colloid, we speak of degree of dispersion, electric density of the surface charge, potential difference of the double layer. A certain approximation to both cases was represented by Gouy's conception in which he ascribed to the double layer a diffuseness and, therefore, instead of dealing with an electric surface density he dealt with a space density of ions and accordingly with concentrations. But these are not homogeneous, being rather, like all the properties of a colloidal solution, periodically varying in any given direction.

* Here Michaelis renounces the view supported by J. Duclaux. See this volume, p. 515. J. A.

12. ORIENTED AND EXCHANGE ADSORPTION; ACIDOID THEORY

The electric charge of colloids, in general, may thus be traced back to an electrical double layer. The question now arises as to what is the inner mechanism or chemistry by which the arrangement of the electricity is brought about. Evidently forces must act which tend to counteract the tendency of the elementary electric charge so to dispose itself that the electrical energy will be a minimum. It seems to me that this cause may be traced back directly to three principal causes, of which we shall first consider two. We may designate them as (1) formation of the double layer through *oriented adsorption*, and (2) formation of the double layer through the *dissociation tendency* and *exchange adsorption*. The third mechanism will receive special attention.

A. Oriented Adsorption.

The conception of oriented adsorption goes back to an idea of Haber's. As is known, the ions of a crystal become fixed in position by residual valences of electrical origin. Thus the valence of a sodium atom in the NaCl crystal previously assumed to be unitary, is, according to present-day views, split up into six partial valences projecting into the three dimensions of space, extending in opposite directions each way from the Na ion, and binding six Cl ions. Consequently the outwardly-pointing partial valences in the surface layer of Na ions are still unattached and are ready to bind to the surface negative ions of the surrounding solution. Thereupon follows anew the formation of a second electrical layer (according to Gouy to be considered as diffuse) outside of the crystal, that is, within the liquid, movable part of the solution. The best example which has been experimentally investigated is that discovered a long time ago by Lottermoser and more recently by Fajans. If, for example, $AgNO_3$ solution is mixed with KI solution, a precipitate of AgI is formed, which at first tends to remain in colloidal solution, and is found to be positively charged. If, further, the quantity of KI added is accidentally equivalent to the $AgNO_3$ the precipitate agglomerates rapidly and is then electrically neutral. If this neutral point is exceeded by a rapid addition of an excess of KI, then the agglomeration is suppressed and the precipitate is charged positively. Lottermoser was able to show analytically that the negative AgI held $AgNO_3$ adsorbed and that the positive AgI held KI adsorbed. The explanation is now simple according to Haber's conception: If an excess of Ag ions are in solution, these will be adsorbed by the AgI to a greater degree than the I ions; whereas if there is an excess of KI in solution the I ions will be the more strongly adsorbed. The "indifferent" point does not necessarily lie exactly at the point of chemical equivalence; rather the isoelectric point corresponds to a definitely determined concentration relation between the I and Ag ions in the solution. For instance, solid $BaSO_4$ is positively charged in a $BaCl_2$ solution, and negatively in a Na_2SO_4 solution; and the isoelectric point is not given in a suspension of $BaSO_4$ in pure water (which contains equal amounts of $Ba^{\cdot\cdot}$ and $SO_4^{=}$ ions defined by the solubility of $BaSO_4$), but in a $\frac{m}{2000}$ Na_2SO_4, according to Gyemant[39] and to Michaelis and Dokan.[40]

In the case of such oriented adsorption the electric density, the potential difference, and the (mean) separation of the two components of the double layer may vary according to conditions in such a way, of course, that one of the quantities is always dependent on the two others. I should like especially to emphasize this point, because I can here recognize an essential difference from the second type of double layer which is to be described presently. Haber's idea applied at first to crystals, but there is no reason to believe that it should not be applied to amorphous aggregates as well, and perhaps better than to crystals.

B. Dissociation Tendency.

The theory of the dissociation tendency was first propounded by the writer in 1910 with some errors, however. Today I would give it the following exposition: there is a large number of evidently hetero-polar compounds, peculiarly prone to electrolytic dissociation, in which one of the ions resulting from dissociation is incapable of existence in the molecularly dispersed dissolved state. An example is silicic acid and the silicates. The probable anion of silicic acid is of old known as a lazy ion with undeterminably small mobility and a poorly defined solubility, on account of the slowness with which equilibrium is established, etc. The matter may be visualized much better in the following way. The dissociation tendency of silicic acid is the same as that of any acid; however, the resulting silicic acid ions do not become molecularly dispersed, but remain bound up in colloidal aggregates. If a particle of silicic acid is placed in water, its dissociation tendency is made evident by the fact that the particle splits off H ions at its surface which arrange themselves as the outer component of the double layer, while the surface layer of ions of the silicic acid which remain bound to the particle, form the inner component of the double layer. If there are in solution any truly dissolved electrolytes, then the H ions of the outer component may be partially or wholly replaced by other cations. According to the previous discussion, this is equivalent to exchange adsorption.

The dissociation of a colloidal solution may be represented in the sense that not all of the surface layer of acid molecules in the aggregate split off H ions and one may speak under the circumstances of a "partial dissociation" and a "degree of dissociation" of the acid. Since, however, according to Gouy we nevertheless are forced to ascribe a special depth to the H-ion layer, and to replace the latter by an imaginary flat H-ion layer placed at the electrical center of gravity, if we still intend to apply in the main the Helmholtz conception of the double layer, we may just as well say that the colloidal acid is always completely dissociated, like the molecule of a crystal or of a true acid (in the sense of Hantzsch) according to Bjerrum's theory—and the more or less complete splitting off of H ions is then expressed by Gouy's modification of Helmholtz's idea, namely, the conception of a flat section of the double layer, having a variable thickness changing with conditions. This leads to the consequence that for a given colloidal acid only the thickness and the potential difference between the two components of the double layer are variable, not its electrical density. The latter is determined rather only by the number of acid molecules laid on the surface. The changes which the electrical properties of the double layer can undergo as the result of exchange adsorption, can be traced back to the change in *thickness* of the double layer, which in its turn results in a change in the potential difference, while the potential difference for a given density is inversely proportional to the thickness. A strongly adsorbed ion, then, is an ion which, by exchange with the H ions of the silicic acid anion layer, forces itself closer than the H ion. It is immediately evident that polyvalent ions force themselves more closely to the anion nucleus than univalent ions, because they exert a small osmotic repulsive force against the electric forces, for an equal number of elementary electric charges. This corresponds to the fact that the adsorbability of ions depends to a great extent upon their valence. These ideas may be applied not only to silicic acid, but also, for instance, to resinous acids like mastic, as well as to the so-called metallic hydroxides prepared in the wet way, which especially in view of the recent researches of Wo. Pauli, do indeed hold complex ions at their surface with the sharing, for example, of Cl; ions which are unknown in the dissolved state, and evidently are capable of existence only in the colloidal form and possess no definite solubility.

These substances collectively form, in consequence, a peculiar group among electrolytes—the electrolytes with a "lazy" ion. As in the case of pure electrolytes, they may be divided into acidoids, the basoids, and the ampholytoids. As acidoids we have learned to recognize the above examples, we may add to them the fatty acids which, considering the beautiful investigations of McBain as a basis, merge from the true acids more and more into acidoids the longer the carbon chain. Of ampholytes there are numerous examples, on the one hand in albuminous colloids; among these there appear to be, as in the case of the fatty acids, all gradations from the almost typically true ampholytes (serum albumin, ovalbumin, hæmoglobin) to the unmistakable ampholytoids (denatured albumin, insoluble albuminous substances like silk and keratin). It is striking that up to the present it has been impossible to find an example of a basoid, that is, of a positively charged colloid which does not become negative in sufficiently alkaline solution. Those metal hydroxides which do not have an amphoteric character, such as KOH, $Ca(OH)_2$, have on the whole no tendency to enter the colloidal state.

13. Potentials as the Result of Spontaneous Distribution of Ions at the Free Surface

The previously discussed modes of potential formation could all be understood on the basis of forces which also are recognized elsewhere in *chemistry;* residual valence in oriented adsorption, and dissociation tendency in the other form. In both cases we may ascribe the cause to a force whose origin lies in the material of the dispersed phase or of the wall. Now there is a series of phenomena which cannot be explained in this manner. Thus experience has shown that in general an electrical double layer is set up as well at the boundary of substances which are entirely unreactive chemically and incapable of dissociating; for example, at the boundary between aqueous solutions and cellulose, collodion, and even gas or air bubbles. The striking part about this phenomenon is that the non-aqueous phase is always negatively charged with respect to the aqueous. Coehn has proposed the rule that every phase is negatively charged with respect to another phase of higher dielectric constant. This rule certainly is not correct in general, otherwise there scarcely could be any substances which become positively charged with respect to water with its very high dielectric constant; but of these there are many. The rule appears capable of more satisfactory application if it is confined to substances which, on account of their chemical nature, display no tendency to ionize. Nevertheless, we do not as yet know enough about charge-development at any interface, and we must be content preliminarily with simply the following rule as the only certain one: all substances of an electrochemically inert nature always become negatively charged with respect to the aqueous phases. The slight exceptions to this rule which thus far have become known will be considered presently. Even under conditions such that electrolyte-like solid phases, which in general appear negative, become positively charged, inert substances almost always retain their negative charge. Thus, for example, glass, kaolin or mastic—which almost always are negative—are at first discharged by Al salts in extremely low concentrations, and become charged with the opposite sign only in moderately high concentrations. On the other hand, cellulose or collodion become completely discharged in high Al concentrations, but whether any reversal of charge occurs is very doubtful; at least the magnitude of the charge is scarcely greater than the experimental error of the measurements. These results were obtained in my laboratory by Gyemant, for cellulose, agar, collodion, and more recently by Jacques Loeb for collodion and a few other substances. Only by means of tetra-valent thorium was Loeb able to show a + charge on collodion. These results were different only if the collodion had previously been in contact with an albumin solution. The collodion thereby became coated with a film of albumin which could not be washed off, and the surface assumed all the amphoteric properties of an albumin solution. However, in all cases where such an irreversible coating was not formed and an effective collodion surface was exposed, the previously described phenomena prevailed. Further, the phenomena of ballo-electricity lead us to suppose that even the free surface of a liquid can show a potential difference, compared with its interior. If, therefore, we seek to explain this potential difference principally through the formation of an ion-double layer, then it remains simply to accept the fact that an inert surface also can "adsorb" ions. According to the definition previously given, this can be only an "apparent" adsorption, that is, the forces effecting the adsorption lie in the solution itself, while the so-called "adsorbent" is entirely non-participating. A few years ago I set up the following working hypothesis in the attempt to explain these phenomena. It is necessary merely to assume that the OH ions of water are more capillary active than H ions. Then it is at least conceivable why the surface of all inert substances is negative toward pure water. Loeb formulated a similar thought in the following way: he employed Langmuir's theory that many unsymmetrical molecules tend toward a certain orientation in the surface. Now Loeb assumed that the water molecules were oriented in the surface with their OH groups outward. Regarding the influence of electrolytes on potential, he found the following. For inert substances like collodion, graphite, and gold, cataphoresis experiments showed that a negative potential always exists toward the purest water obtainable, but scarcely exceeded a value of about 7 millivolts. This potential was now strengthened by the addition of numerous electrolytes. The effect of the electrolytes was to carry the potential, with increasing concentration through a maximum, which seldom exceeded 60 millivolts. By varying the anion, the negative effect of the same increased with its valence; if the cation was varied, the negative effect of the electrolyte decreased with the valence. In general, the maximum attainable potential was about 60 millivolts in the highest case and 0 in the lowest. With trivalent lanthanum a doubtful charge on the positive side was observed in the highest concentration, and only tetravalent thorium produced an energetic + charge in low concentrations. This specific nature of thorium was previously observed by M. C. Taggart in its effect on the charge at the surface between aqueous solutions and air bubbles. In any case, up to the trivalent ions, a definite positive charge is not producible on these inert substances, and this seems to me to be the essential point of difference from dissociating surfaces; for glass and all silicates as well as mastic, become strongly positively charged by trivalent ions even in very small concentrations.

The charging effect of electrolytes at inert boundaries is not explained on the basis of any of the earlier developed theories; and it is necessary to conclude, therefore, that it rests on a distribution tendency of the ions independent of any simultaneous action of the inert surface.

14. The Isoelectric Point

We have repeatedly mentioned the fact that many colloids can be discharged by certain electrolytes. When the concentration of these electrolytes is gradually increased from 0, a certain concentration must be reached at which the charge is equal to zero. The colloid is then at the isoelectric point. To define the isoelectric point for a given colloid, it is sufficient therefore to state the concentration of the electrolyte at which the charge is equal to zero. The isoelectric point furthermore varies with the nature of the discharging electrolyte. We have seen that the discharging of a colloid almost never occurs except if a polyvalent ion, especially a polyvalent cation, is involved. Hydrogen and OH ions are the only univalent ions which can produce discharge. This case occurs quite frequently, however, and has a very important practical as well as theoretical bearing, while for physiology the discharging power of H and OH ions is of quite special significance, because tri- and tetra-valent cations never occur under physiological conditions. When we speak of the iso-electric point, we mean, as a rule, that concentration of H ions at which this reversal of charge appears. Now, to be sure, all other univalent ions have some influence on the charging of colloids, and if, in general, they cannot produce a charge, nevertheless it is to be expected that they have an influence on the p_H value necessary for discharge. But in practice it is not possible to change the H ion concentration of a solution without simultaneously changing the concentration of other ion species, and consequently it seems at first glance an unsatisfactory proceeding to define isoelectric point as that of the H-ion concentration necessary for reversal of charge. On the contrary, however, I have been led to conclude that in numerous instances the H-ion concentration required for reversal is practically uninfluenced by the presence of numerous other ions in moderate concentration, provided they are not of the extremely active type like trivalent metal ions or alkaloid ions. I have been able to acquire this information, for example, for denatured and genuine serum albumin, gelatin, casein, hæmoglobin, and others; all purely albuminous substances as will be noted. The various H-ion concentrations were produced, as a rule, by mixing weak acids with their alkali salts which I called *regulators.* Mixtures according to the same principle were produced about the same time by Sörensen, and were given by him the present widespread name of *buffers.* I can now show that within rather wide limits, the H-ion concentration which characterizes the isoelectric point, is independent of the kind and concentration of the buffer solution. Of course this cannot apply to every sort of buffer, but it has been shown, for example, that for an albumin solution the isoelectric point lies at practically the same H-ion concentration whether the buffer is produced from acetic acid, propionic, lactic, laevulic, cacodylic acids, or phosphates. On the other hand, when citrate buffers are used a significant departure is observed. From the consistency of these various methods, one may conclude that with all these buffers, so far as they show agreement, the influence of the H ions, as determined, outweighs practically completely that of the other ion species. And thus for each chemically characteristic type of albumin, we can assign a characteristic isoelectric point which is just as much an attribute of the substance as, say, its melting point. If then, we define isoelectric point from now on in the above sense, and inquire which sort of colloids principally have such a point and which not, then we find without exception the following: all colloids which on account of their purely chemical behavior must be considered as amphoteric substances, forming salts with acids as well as with bases—possess an isoelectric point. On the other hand, all substances which chemically are non-amphoteric ("einsining") do not possess an isoelectric point. Here we are confronted with a question we have already dealt with from another viewpoint.

16. THE DONNAN POTENTIAL *

As a result of the work on Jacques Loeb, the question of the Donnan potential in the colloidal state has become one of lively interest. We are discussing here only the *general* aspects of the problem.

A large number of electrical phenomena in colloids may be advantageously treated by means of a thermodynamical method first considered by Donnan.[32] Imagine two electrolyte solutions separated by a membrane permeable for all ions except one, which is in solution I but not in solution II. Such a membrane, for example, is collodion, which is impermeable to Congo-red ions. Suppose Congo-red is present in solution I as its Na salt, and that NaCl is also present. Diffusion leads to an equilibrium, which we may analyze as follows:

In solution I are ions of Congo-red R^-, Cl^-, and Na^+; in solution II only Cl^- and Na^+. From the basic law of electrical neutrality, the following equation must apply to solution II:

$$[Na^+]_{II} = [Cl^-]_{II} \tag{1}$$

and in solution I

$$[Na^+]_I = [Cl^-]_I + [R^-]. \tag{2}$$

Therefore in I $[Na^+]_I$ cannot equal $[Cl^-]_I$, and $[Na^+]_I$ cannot equal $[Na^+]_{II}$.

The equilibrium conditions may be determined on the basis of thermodynamics. The equilibrium is characterized by the fact that by isothermal and reversible transport of a very small quantity of NaCl from one solution to the other, no work is caused. If *dn* moles NaCl are transported, then *dn* moles of Na^+ ions and *dn* moles of Cl^- ions must be simultaneously transported in the same direction. The former gives an amount of work $dn.R.T.ln\,\frac{[Na^+]_{II}}{[Na^+]_I}$, the latter $dn.R.T.ln\,\frac{[Cl^-]_{II}}{[Cl^-]_I}$.

The sum of both these amounts of work must equal zero, hence

$$[Na^+]_{II} \,.\, [Cl^-]_{II} = [Na^+]_I \,.\, [Cl^-]_I. \tag{3}$$

The equations (1), (2) and (3) contain five different quantities. Assuming that $[R^-]$ is given, and that in addition one of the other quantities is known, the three others may be determined directly from these three equations. In this manner we can determine in each solution the equilibrium concentration of each individual ion, and furthermore the total molecular concentration and therefore, *e.g.*, the osmotic pressures in each solution.

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* This section translated by J. Alexander.

So far as electrical phenomena are concerned, we are interested only in the calculation of the potential difference between the solutions. The origin of the potential difference may be considered qualitatively as follows: Since at equilibrium solution I has more Cl^- ions than solution II, there is a tendency for Cl^- ions to move from I to II. But since transfer would destroy electrical neutrality and give rise to a difference in potential between I and II, it can occur only to an indeterminably small extent, in fact only to such an extent that the electrical potential difference caused thereby would just counterbalance the diffusion pressure. On the other hand, the Na^+ ions try to move from solution II to I, that is, in the opposite direction. Since, however, they have the opposite charge, they give rise to a potential difference of the same sign. This potential difference can likewise be calculated quantitatively from thermodynamic considerations. For this purpose, let us imagine that a very small amount of positive electricity is transported from I to II. Our unit of electrical quantity is 96,540 Coulombs $= F$, and we will assume that a very small quantity $dn \,.\, F$ is transported. This transport is brought about by the migration of several positive Na^+ ions from I to II, and several negative Cl^- ions from II to I. Both kinds of ions take part in the transport, according to their respective mobilities, U and V; the Na ions have a part $\frac{U}{U+V}\,dn$, and the Cl^- ions a part $\frac{V}{U+V}\,dn$.

The osmotic work which yields the Na ions is

$$\frac{U}{U+V}\,dn \,.\, R.T.ln\,\frac{[Na^+]_{II}}{[Na^+]_{I}},$$

and the osmotic work of the Cl ions is

$$\frac{V}{U+V}\,dn \,.\, R.T.ln\,\frac{[Cl^-]_{I}}{[Cl^-]_{II}}.$$

Now, according to (3),

$$\frac{[Na^+]_{II}}{[Na^+]_{I}} = \frac{[Cl^-]_{I}}{[Cl^-]_{II}}$$

and the sum of the osmotic work is therefore

$$\frac{U}{U+V}\,dn \,.\, R.T.ln\,\frac{[Na^+]_{II}}{[Na^+]_{I}} + \frac{V}{U+V}\,dn.R.T.ln\,\frac{[Cl^-]_{I}}{[Cl^-]_{II}} = dn \,.\, R.T.ln\,\frac{[Na^+]_{II}}{[Na^+]_{I}}.$$

Let E represent the potential difference; then the electrical work in this transport is $dn \,.\, E \,.\, F$. The sum of the electrical and the osmotic work is 0, therefore

$$dn \,.\, E \,.\, F = dn \,.\, R.T.ln\frac{[Na^+]_{II}}{[Na^+]_{I}}, \text{ whence}$$

$$E = \frac{R.T.}{F} \,.\, ln\,\frac{[Na^+]_{II}}{[Na^+]_{I}} = \frac{R.T.}{F} \,.\, ln\,\frac{[Cl^-]_{I}}{[Cl^-]_{II}}. \qquad (4)$$

Formula (4) has the following significance: once we determine the concentration relations of *either one* of the diffusible ions, we can find the potential difference from (4).

The assumption on which this deduction is based was that a single electrolyte, NaCl, was present in addition to the non-diffusible ion, and that it has two monovalent ions. The argument may be generalized and extended to a mixture of any number of electrolytes and ions of any valency. We will assume that in solution I the non-diffusible ion, which may have any desired valency, is present in the equivalent concentration $[R^-]$. In addition let there also be in solution I various cations in the molar concentration $[K_1^+]_I$, $[K_2^+]_I$, etc. Let the valencies of these cations be γ_1, γ_2 . . . . Let there be present various anions in the molar concentrations $[A_1^-]_I$, $[A_2^-]_I$ . . . , whose valencies are α_1, α_2 . . . . Then the electrical neutrality of the solution demands that

$$\gamma_1[K_1]_I + \gamma_2[K_2]_I + \ldots = \alpha_1[A_1]_I + \alpha_2[A_2]_I + \ldots + [R^-].$$

In solution II electrical neutrality requires that

$$\gamma_1[K_1]_{II} + \gamma_2[K_2]_{II} + \ldots = \alpha_1[A_1]_{II} + \alpha_2[A_2]_{II} + \ldots .$$

Comparing these two equations and remembering that the right side of the first equation contains the member $[R^-]$, it is obvious that the concentration of the individual diffusible ions in I and II cannot be equal to each other. The balance is characterized by the fact that in the transport of dn equivalents of any selected *electrolyte* from I to II, the osmotic work must equal 0. We must here say *electrolyte,* and not *ion,* because the transport on one kind of ion involves electrical work. The dn equivalents of any selected electrolyte contain $\frac{1}{\gamma}\,dn$ cations of a valency of γ, and $\frac{1}{\alpha}\,dn$ anions of a valency of α.

If we remove one equivalent of any particular electrolyte, whose cations at equilibrium have the concentration $[K]_I$ and $[K]_{II}$ respectively, the transport of the cations requires the work $\frac{1}{\gamma} \,.\, dnRT \,.\, ln\,\frac{[K]_{II}}{[K]_I}$

In like manner the transport of the anions belonging to these cations requires the work $\frac{1}{\alpha} \,.\, dn \,.\, RT \,.\, ln\,\frac{[A]_{II}}{[A]_I}$.

The sum of these two amounts of work must be 0; therefore

$$\left(\frac{[K]_{II}}{[K]_I}\right)^{\frac{1}{\gamma}} = \left(\frac{[A_I]}{[A_{II}]}\right)^{\frac{1}{\alpha}}, \tag{5}$$

Now we may regard the combination of the first cation with the first anion as an "electrolyte," or just as well the combination of the first cation with any other anion. The formation of an electrolyte from a pair of ions is arbitrary, and for each electrolyte the formula (5) must apply. It therefore follows throughout that

$$\left(\frac{[K_1]_{II}}{[K_1]_I}\right)^{\frac{1}{\gamma_1}} = \left(\frac{[K_2]_{II}}{[K_2]_I}\right)^{\frac{1}{\gamma_2}} = \cdots = \left(\frac{[A_1]_I}{[A_1]_{II}}\right)^{\frac{1}{\alpha_1}} = \left(\frac{[A_2]_I}{[A_2]_{II}}\right)^{\frac{1}{\alpha_2}} = \ldots \tag{6}$$

If we designate the concentration ratio of any monovalent cation in I and II by r, then the relation of any cation having a valency of $\nu = r^{\frac{1}{\nu}}$, and of any anion having a valency of $\nu = \left(\frac{1}{r}\right)^{\frac{1}{\nu}}$.

To calculate the potential difference between I and II, imagine that dn equivalents of positive electricity are transferred from I to II. This transfer can take place only by the simultaneous transfer of a certain amount of each kind of cation from I to II, and of a certain quantity of each kind of anion from II to I.

Let the total amount of electricity transferred be $dn \,.\, F$ coulombs. Each individual kind of anion shares fractionally in the transfer to the extent demanded of it by the transference number fixed by the conditions.

If $u_1, u_2, \ldots$ are the transference numbers of the individual cations, and $v_1, v_2 \ldots$, those of the anions, then

$$u_1 + u_2 + \ldots + v_1 + v_2 + \ldots = 1. \tag{7}$$

The transfer of $u_1 \,.\, dn$ equivalent cation of the first variety involves the osmotic work

$$\frac{1}{\gamma_1} \,.\, u_1 \,.\, dn \,.\, RT \,.\, ln \frac{[K_1]_{II}}{[K_1]_I} = u_1 \,.\, dn \,.\, RT \,.\, ln \left(\frac{[K_1]_{II}}{[K_1]_I}\right)^{\frac{1}{\gamma_1}}$$

A similar expression applies to the other cations. The transfer of the first variety of anion involves the work

$$v_1 \,.\, dn \,.\, RT \,.\, ln \left(\frac{[A_1]_I}{[A_1]_{II}}\right)^{\frac{1}{a_1}},$$

and similarly for the other anions.

Now since according to (6) the expressions affected by the logarithmic sign are equal to each other, the total osmotic work is

$$(u_1 + u_2 + \ldots + v_1 + v_2 + \ldots) \,.\, dn \,.\, RT \,.\, lnr^{\frac{1}{\nu}}.$$

According to (7), the parenthetical expression $= 1$, and therefore the total osmotic work involved in the transfer of all the ions equals $dn \frac{RT}{\nu} . \, lnr$, wherein r denotes the relative concentration of any variety of positive ion in II and I, or that of any variety of negative ion in I and II, and ν denotes the valency of such ions.

The electrical work here involved is $dn \,.\, F \,.\, E$. It equals the osmotic work, and therefore the potential difference E is

$$E = \frac{RT}{\nu \,.\, F} \,.\, lnr.^{*} \tag{7a}$$

For a temperature of 20°, using Briggsian logarithms (having a base of 10)

$$E = \frac{1}{\nu} \,.\, 58 \log_{10} r \text{ millivolts.}$$

It is of interest to see what influence on the potential is exerted by a variation in the concentration of the impermeable ions as well as of the individual permeable electrolytes. We will take up the calculation only for monovalent ions, and to establish definite conditions, we will assume the impermeable ion is a cation and that it is present in the equivalent concentration q. In addition suppose there is present one monovalent electrolyte, and that the concentrations of the anions is a_I and a_{II} respectively, and of the cations k_I and k_{II} respectively. Electrical neutrality requires that

$$q + k_I = a_I. \tag{8}$$

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* *ln* means natural logarithm or $\log_{\epsilon}$. J. A.

From the equilibrium conditions above given we have

$$k_I \,.\, a_I = k_{II} \,.\, a_{II}$$

$$\text{or } k_I \,.\, a_I = a^2_{II}. \tag{9}$$

From (8) and (9) we have the quadratic equation

$$a^2_I - q \,.\, a_I - a^2_{II} = 0.$$

Solving this for a_I we get

$$a_I = \frac{q}{2} + \sqrt{\left(\frac{q}{2}\right)^2 + a^2_{II}}. \tag{10}$$

The other possible root of the equation, having a minus sign, has no physical significance, because when $q = 0$, $a_I = a_{II}$, but does not become equal to $-a_{II}$. Solving for a_{II}, we get

$$a_{II} = \sqrt{a^2_I - a_I q}. \tag{11}$$

Substituting in (8) the value for a_{II}, we have

$$k_I = -\frac{q}{2} + \sqrt{\left(\frac{q}{2}\right)^2 + a^2_{II}}. \tag{12}$$

Solving (8) and (9) for k_{II}, we get

$$k_{II} = \sqrt{k^2_I + k_I q}. \tag{13}$$

Comparing (10) and (12) it is obvious that $a_I > k_I$.

The difference becomes greater in proportion as q is greater. If we wish to see the influence of variation of the diffusible electrolytes, we have from (13)

$$\frac{k_{II}}{k_I} = \sqrt{1 + \frac{q}{k_I}}$$

Therefore,

$$E = \frac{RT}{2F} \ln\left(1 + \frac{q}{k_I}\right). \tag{14}$$

If we vary the total quantity of diffusible electrolytes, k_I must likewise vary in the same direction. Now (14) shows that E is a symbate function of k_I and therefore of the total quantity of the diffusible electrolytes, running on without maximum or minimum. The smallest conceivable value of k_I is 0, which exists when the total amount of diffusible electrolytes $= 0$. In this case, according to (14), $E = \infty$. The greatest conceivable value for k_I is ∞, which exists when the total amount of diffusible electrolytes is ∞. Then $E = 0$. From this it is evident that as the total amount of diffusible electrolytes increases, the potential verges toward 0.

The next question to consider is how the potential is affected when one diffusible ion is only partially substituted by another of the same valency and the same charge. Assume that a non-diffusible cation is present in solution I in a concentration q; in addition let an anion be present in the concentrations a_I and a_{II} respectively, and two different monovalent cations in the concentrations l_I, l_{II} and m_I, m_{II}. Then the following equations apply:

$$(1)\quad l_1 + m_1 + q = a_I$$

$$(2)\quad l_2 + m_2 = a_{II}$$

$$(3),\ (4)\ \frac{l_{II}}{l_I} = \frac{m_I}{m_{II}} = \frac{a_I}{a_{II}}.$$

Assuming that three of the seven variables in these equations are given, that is, q, a_I, l_I, the other four unknowns can be calculated as functions of the three known quantities. Thus, *e.g.*, solving for a_{II}, we get

$$a_{II} = \sqrt{a^2_I - a_1 q}.$$

In this equation neither l_I or l_{II} occur, and the result is the same as if, in place of the two cations, there was a single one of the same total concentration. Thus we also have

$$\frac{a_{II}}{a_I} = \sqrt{1 - \frac{q}{a_I}}$$

and therefore the potential is independent of how the concentration of cations is distributed with reference to the two cations.

This has the following significance: the potential is unaffected if one diffusible ion is replaced by a mixture of different kinds of ions having the same charge and valency. This brings to light the fact that the potential is independent of the chemical individuality of the ions, but is determined solely by their valency and the sign of their charges.

All our previous deductions were founded on the basic assumption that in the reversible and isothermal transport of 1 mol of ions from a solution in which their concentration is c_I to a solution in which their concentration is c_{II}, the amount of work involved is

$$RTln\frac{c_{II}}{c_I}.$$

This assumption is only approximately correct. In reality in place of the molar concentrations, we should use the thermodynamic activities in the sense of G. N. Lewis, whereas in all those equations which express the electrical neutrality of the solutions, *e.g.*, equations (1) and (2), the concentrations must remain. This will involve a change in the distribution of the ions in such a manner that, *e.g.*, in equation (6) we must include everywhere within the square brackets the factor involving activity instead of that involving concentration.

According to G. N. Lewis and N. Bjerrum, concentration may be converted into activity by multiplying by an activity factor *f*, which in the case of very dilute solutions with nothing but monovalent ions, is practically equal to 1. With increased concentration of electrolytes, especially in the presence of polyvalent ions, there appear perceptible variations from equation (6), if we use concentrations instead of activities.

There are no experiments along this line, but the following conditions seem to mitigate the variations to be expected. In the first place, as we have shown, the larger and definitely measurable potential differences are obtained only if the electrolyte concentration is small. In this case, however, the variations are small. Secondly, in the analysis of the distribution equilibrium, especially in the investigations of Jacques Loeb, there is generally used a method which measures the activity of ions and not their concentration. Thus, for example, the H-ion concentration in both solutions, and sometimes the Cl-ion concentration, are determined by potentiometric measurements.

In the case of H ions we measure the so-called p_H, and this quantity is not, as has been previously assumed, the negative logarithm of the *concentration* of H ions, but of the thermodynamic *activity* of H ions. Thus the error involved in the theory of the authors was sometimes unintentionally corrected by the experiment itself. Since writing this, Hückel [42] has developed this matter.

The most complete confirmation of the Donnan theory is found in the experiments of Jacques Loeb,[33] who used gelatin in acid solution as the non-diffusible cation, and collodion as the semi-permeable membrane. A 1 per cent solution of gelatin with varying amounts of HCl was placed in a collodion bag and dialyzed against pure HCl until equilibrium was reached. Then the external and the internal concentrations (really activities) of H ions and of Cl ions were determined, and in addition the potential difference between the outer and the inner solutions across the membrane was measured electrometrically. The two solutions were connected by means of a capillary tube filled with KCl solution, each in connection with a calomel electrode; and these were connected with an electrometer.

There was satisfactory agreement between the potential difference measured directly, and that calculated from the equilibrium analytically measured. The theory finds increased application in that it may be carried over to cases in which strictly speaking there is no membrane present. The application of the theory to such cases began with the experiments of Procter [34] on the swelling of gelatin jellies in dilute solutions of HCl and led to the theory of solution of Procter and Wilson,[35] and further of Wilson and Wilson.[36]

The authors assume that gelatin under conditions where it does not dissolve but only swells, is permeated by the outer solution in such wise that a similar ion balance is formed as in true membrane experiments.

If the solution contains, *e.g.*, HCl, the gelatin molecules bind H ions by means of their NH_2 groups,* and thereby become positive ions with an NH_3^+ group. These positive gelatin ions are, however, not diffusible, but form the framework of the jelly. Because of their cohesion they cannot diffuse into the outside solution, just as in experiments with a truly fluid solution of gelatin within a membrane, the gelatin ions are prevented by the membrane from diffusing into the outer solution. The conditions for the production of a Donnan equilibrium are therefore the same as in a membrane experiment, and there must in like manner arise a potential difference between the interior of the gelatin and the outer solution.

The theory was extended still further by Jacques Loeb by assuming that the Donnan equilibrium also governs the distribution of ions between the individual microscopic or ultramicroscopic colloidal micells of a colloidal solution, and the dispersion medium. A capital support for this view was found by Loeb in the fact that, within the limits of experimental error, the colloidal degree of dispersion of protein solutions is determined exclusively by type of charge and by the valency of the ions, while their chemical character is without influence. For the conditions governing his experiments, Loeb has doubtless proven the correctness of this view. That is no reason why, however, under other conditions, especially with more highly concentrated solutions of electrolytes, the chemical individuality of the ions may not come into evidence, and ions of like charge and valency have different actions on the colloidal condition, which expresses itself in the lyotropic Hofmeister series.*

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* This simple explanation is obviously not so, since Blasel and Matula found that *deaminized* gelatin bound about as much acid as the original gelatin with its amino groups intact. J. A.

It must be recalled that similar phenomena occur in all ion activity, which are made more comprehensible by the theory of Debye. In all activities of ions we must distinguish two zones of concentration. In lower concentrations the action of ions depends only on their valency and kind of charge. In higher concentrations, on the contrary, each ion has an individual property, which in the case of symmetrical ions, *e.g.*, monatomic ions, must be conceived of as a function of the ionic diameter.

Details regarding the application of the Donnan theory to colloids in the sense of Jacques Loeb are given elsewhere in this book.

The Donnan theory of membrane potential is valid only when thermodynamic equilibrium is established between two solutions separated by the membrane, *i.e.*, when all possible diffusion processes have taken place completely. There is another possibility of a membrane being efficient electrically, when the two solutions separated by the membrane are not in equilibrium, but a diffusion is occurring across the membrane. This question has just been treated by L. Michaelis.[41]

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* This has been proven by the work of W. A. Hoffman and R. A. Gortner, 2nd Colloid Symposium Monograph, Chem. Catalog Co., 1925. J. A.

The Specific Inductive Capacity of Substances in the Colloidal State

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It is agreed[1] that the specific inductive capacity of matter may be attributed to two effects: first polarization by orientation or displacement of heavy and charged particles (atoms, molecules, or molecular groups), and second by the movement of electrons in the interior of each particle, which determines polarization.

We have elsewhere described[2] the facts which led to the idea of specific inductive capacity and the methods usually employed to measure it. This electrical property of matter is generally defined thus: the specific inductive capacity of a medium is equal to the capacity of a condenser containing this medium, compared with the capacity of the same condenser containing air—strictly speaking, void.

I. *Since in a colloidal system the dispersion medium and the dispersed phase are generally not the same, we will first consider the question whether a colloidal system has a specific inductive capacity different from that of the dispersion medium.*

A. The Dispersion Medium is Liquid

In this case the most rational comparison is that between the specific inductive capacity of the solution, and that of the ultrafiltrate.

We will follow the classification of colloidal solutions into "highly solvated" and "slightly solvated" according to the equilibrium between the dispersion medium and the dispersed phase.

(1) "Slightly Solvated" Solutions.

(a) *Non-aqueous Dispersion Medium.*—In 1897 Millikan[3] studied the specific inductive capacity of an emulsion of water in a mixture of benzene and chloroform. He considers the water droplets as conductors suspended in an insulator, and tried to verify the formula of Clausius-Mosotti

$$k = k' \frac{1 + 2x}{1 - x}$$

where k is the specific inductive capacity of the emulsion, k' that of the insulating dispersion medium, and x the ratio between the volume of the dispersed phase and the total volume. Millikan studied solutions whose concentration reached as high as 17.7 per cent, the ratio $\frac{k}{k'}$ being between 1 (for the dispersion medium alone) and 1.5; a satisfactory agreement with the theoretical formulæ was found.

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* Translated by Jerome Alexander. Specific Inductive Capacity is Dielectric Constant.

We have measured [4] the specific inductive capacity of alcosols of platinum (0.22 per cent), of gold, of cadmium (0.2 per cent), prepared at — 80° according to Svedberg's method. These sols had a specific inductive capacity of about 1 per cent more than that of pure alcohol, but this increase may be accounted for either by condensation of atmospheric moisture during pulverization, or else by a chemical transformation of the alcohol.

(b) *Aqueous Dispersion Medium.*—The inductive capacity of the colloidal solution is the same as that of water in the following cases: [4] sols of benzopurpurine (Grübler) 0.5 per cent; arsenic trisulfide 0.5 per cent; silver sulfide 0.2 per cent; silver (Bredig's method) with 77 and 93 mg. per liter; a fresh solution of soap having a surface tension markedly below that of pure water, a freshly made ferric hydroxide sol, a sol showing Majorana's phenomenon, and an aniline blue sol.

It seems, then, that most colloidal solutions of the "slightly solvated" class have the same specific inductive capacity as the "solvent." However, by studying the sols of vanadic anhydride [5] we have found it an interesting exception in two respects: their specific inductive capacity is very high (a 3 per cent sol has a s.i.c. of 1280, not a maximum value, but about 15 times that of other known liquids), and their specific inductive capacity ("dielectric constant") is not constant. These anomalies are caused by the rod-like shape, and perhaps the structure, of the micells of V_2O_5, which is furthermore the cause of the well-known optical anisotropy of these sols. In order that these optical and electrical phenomena both be produced, there is necessary, according to our experiments, that a directive force be superimposed on the haphazard Brownian motion and orient the micells; the more powerful the directive force, the greater the number of particles oriented, and the higher the specific inductive capacity. The particles are therefore subjected to two antagonistic forces: as these are caused to vary, the specific inductive capacity varies correspondingly. This explains the increase of the specific inductive capacity which tends toward a saturation value when the intensity of the electric field increases, and its rapid diminution as the temperature increases. The current frequency also influences the specific inductive capacity, which may be attributed to the directive effect of the electric field: With high frequencies, corresponding to waves of about 30 m., the dipoles, that is the dispersed phase, have not time enough to orient themselves with each inversion of the current, and therefore the specific inductive capacity is that of the solvent alone. The specific inductive capacity increases in direct proportion to the diminution of the frequency: the particles have time enough to follow the pulsations of the current, so that for a frequency corresponding to a wave of about 100 km. the specific inductive capacity reaches a saturation value, all particles being oriented. Additional variables influencing the specific inductive capacity of sols of vanadium anhydride are concentration, temperature, the age of the solution and the time the current has been traversing it. The two latter factors are comprehensible thus: like all other colloidal solutions, V_2O_5 sols change with age; a freshly prepared sol shows neither double refraction nor increase in specific inductive capacity. The appearance of these phenomena goes hand in hand with a certain phase of this change with time: this phase is the preliminary step toward coagulation, but an extremely slow coagulation during which the particles, as they grow, take the shape of little rods and probably a crystalline structure. The same fact explains why the specific inductive capacity increases with age. It increases under the influence of the electric current which also has a coagulating action and which, so to say, artificially accelerates ageing.

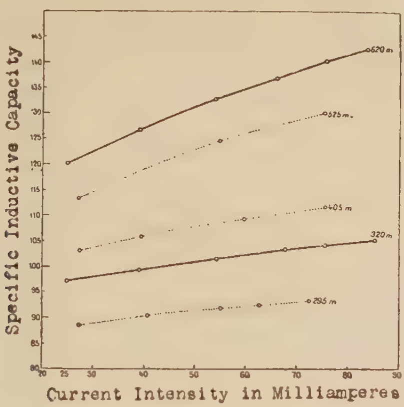

FIG. 1.—Influence of current intensity at different frequencies. Concentration of sols 0.30 and 0.32 grams per liter. Temperature 18°.

The sol of V_2O_5 is an instance where we have combined in characteristic manner these different factors, which are indeed the cause of the specific inductive capacity. According to Debye, the motion of the electrons within the elements constituting water, gives a specific inductive capacity of 4; the

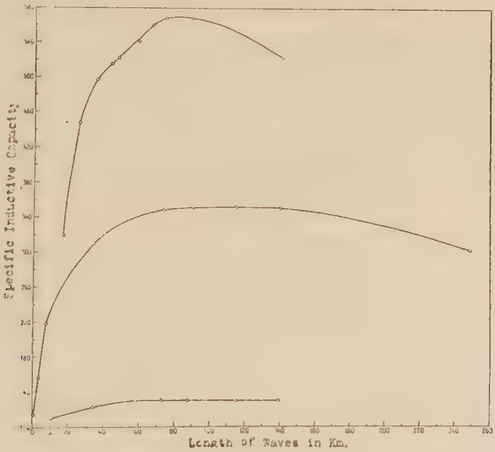

FIG. 2.—Influence of current frequency. Concentration of the 3 sols is 0.0075, 0.03, and 0.06 grams per liter. Temperature 19°.

polarization of the water particles as dipoles, raises the specific inductive capacity up to 81, and finally the orientation of the V_2O_5 rodlets, brings it up to 1300, the value found experimentally.

Below are given two graphs showing certain variation of the specific inductive capacity of V_2O_5 sols.

(2) "Highly Solvated" Solutions.

The specific inductive capacity of these sols usually differs from that of the pure dispersion medium.

Below are given the experimental results, the measurements having been made by Fürth;[6] gelatin had already been studied in 1897 by Drude.[7]

	Per Cent Concentration of Sol.	Specific Inductive Capacity
Lecithin	0.075	77.5
	0.15	74.0
	2.0	76.0
Pepsin	1.0	78.5
	0.5	84.0
Trypsin	0.25	81.5
	0.0	87.0
Gelatin (superfine)	1.9	74.0
	4.8	67.5
	6.7	66.0
	9.1	61.0
	13.0	58.0
	16.6	53.0
	16.6	51.5
	30.0	48.0
	50.0	44.0
Albumin (Kahlbaum)	0.24	76.0
	0.47	69.5
	0.94	67.5
	0.87	58.5
	3.75	52.2
	7.5	45.0
	15.0	32.8
Human blood (before coagulation)		85.5
Human serum (centrifuged from ppt.)		85.5
Horse serum		85.0
Anti-diphtheretic serum		85.0
Guinea pig serum		85.2
Human serum (*a*) untreated		85.5
(*b*) heated ½ hr. at 50°		83.3
(*c*) agitated ½ hr.		81.9
Guinea pig serum (*a*) untreated		85.2
(*b*) heated ½ hr. at 50°		82.8
(*c*) agitated ½ hr.		82.8
Human serum treated with ammonium sulfate (*a*) normal		85.5
(*b*) albumin		82.4
(*c*) globulin		85.2
Human milk		75.0
Human urine		82.8
Human saliva		83.5
Cows' milk		66.0
Cream		63.0
White of hen's egg		68.0
Yolk of hen's egg		60.0

B. Isocolloids

Isocolloids, by definition, are mixtures of more or less associated polymers. A large number of insulators fall into this class.

India rubber (8)	2.76	
Synthetic rubber (8)	2.77	
Ebonite (8)	2.98	
(10)	2.79	
Gutta percha (10)	4.43	
(9)	2.92	—for V = 920
(9)	2.62	— " V = 1,700,000
Vulcanized rubber (9)	2.73	— " V = 920
(9)	2.45	— " V = 1,700,000
Amber (10)	2.8	
Rosin (10)	3.1	
Sealing wax	4.56	
Paraffin (10)	2.52	

C. GLASSES

According to Doelter, a glass may be considered as a colloid, as a desiccated gel. Glasses have been subjected to numerous investigations, but we give only such results as were made on well defined substances. Following Starke,[12] Loewe[11] measured by Drude's and by Nernst's method a series of glasses made by Schott of Jena.

	$\lambda = 0.80$ cm.	$\lambda = 10^4$ cm.
Borate crown (S. 196)	5.05	5.52
Boro-silicate crown (O. 1948)	6.15	6.20
Phosphate crown (S. 169)	6.20	6.40
Barium crown (O. 1610)	7.65	7.83
Barium crown (very heavy) (O. 1922)	7.42	7.69
Silicate crown (O. 1087)	7.10	7.00
Crown with high dispersion	7.70	9.14
Semi-flint (O. 1469)	7.62	7.78
Borate flint (S. 99)	7.63	8.06
Silicate flint (O. 1353)	7.30	8.29

The dispersion is therefore anomalous, that is, the specific inductive capacity increases with the wave length.

In 1917, Jaeger[13] also measured the specific inductive capacity of glasses made by Schott of Jena, employing wave lengths varying from 10 m. to 1.2×10^6 m. He found, on the contrary, there is no variation of specific inductive capacity with the frequency.

		Specific Inductive Capacity
Uviol crown (U.V. 3199)		5.63
Fluor crown (O. 7185)		5.87
Phosphate crown (S. 367)		6.41
Silicate flint (S. 461)		16.45
Flint (O. 118)		7.27
Barium flint, light (O. 1266)		7.67
Crown with high dispersion (O. 381)		6.79
Barium crown, very heavy (O. 1209)		8.35
White Glass II	the chemical composition of these glasses is given	7.16
Black Glass II		7.39
Violet Glass		6.83

A. Gray and J. J. Dobbi[14] using a ballistic method report the following figures:

Chemical Composition	
$22SiO_2$, $5PbO$, $2K_2O$	7.966 at 15° 7.630 " 120°
$17SiO_2$, $5PbO$, $2K_2O$	7.991 " 14°
$28SiO_2$, $16BaO$, $3Al_2O_3$, $9B_2O_3$	8.5

Chemical Composition	
$20SiO_2$, $2ZnO$, $2MgO$, $3Na_2O$, $2B_2O_3$	7.54 at 15°
$43SiO_2$, $5PbO$, $5Na_2O$, $3K_2O$	7.06 " 10° 7.90 " 130°
$10SiO_2$, $3PbO$, $3Na_2O$	5.42 " 8° 5.59 " 130°
$20SiO_2$, $9BaO$, $5K_2O$	6.93 " 22° 7.18 " 147°
$23SiO_2$, $5PbO$, $3K_2O$	7.22 " 18° 7.42 " 142°
$24SiO_2$, $5PbO$, $4Na_2O$	8.013 " 20° 8.302 " 140°

D. GELS AND COLLOIDS IN DRY STATE

	Specific Inductive Capacity
Blood clot	84.0
Frog muscle	83.0
Gray cerebral matter (human)	85.0
White cerebral matter (human)	90.0
Optic nerve (ox)	89.0
Green leaf	83.0
Gelatin	5.6
Egg white (Kahlbaum)	16.3
Night blue	4.4
Congo red	20.0
Methylene blue	18.1
Printers' ink	14.5
Starch	11.6
Dextrin (Kahlbaum)	8.0
Casein (Kahlbaum)	8.0
Hemoglobin (Kahlbaum)	14.2
Cholesterin (Braun)	5.4
Lecithin (Kahlbaum)	13.0
Cellulose [a]	6.8
Normal cellulose triacetate [a]	3.8
Paper for cables (chemical wood pulp without fiber)[a]	
Blotting paper [b]	1.83 for V = 920 1.55 " V = 880,000
Sized paper	4.2
Unsized paper	3.4
Wood [c] (dried 2 hrs. at 170° and cooled under benzene)	
Oak	2.46 3.64
Beech	2.51 3.63

Figures are those of Fürth, unless otherwise indicated.

[a] A. Campbell, *Proc. Roy. Soc.*, 78, 196 (1906)—static method.
[b] C. Bairsto, *loc. cit.*
[c] Starke, *loc. cit.*

II. *Are the physico-chemical properties of a colloidal system affected by the specific inductive capacity of the dispersion medium, or by the difference in specific inductive capacity between dispersion medium and dispersed phase?*

We will first consider the phenomena of the formation and the swelling of colloidal systems. The influence of the specific inductive capacity first manifests itself in the variable dissociative power of the solvent. J. J. Thompson[15] and W. Nernst[16] hold the view that the greater the specific inductive capacity of a solvent (in our case a dispersion medium) the greater in proportion is its dissociating power. This influence plays a rôle in the domain of colloidal dispersion, both in swelling and formation of colloidal solution.

Wo. Ostwald[17] on allowing rubber to swell in various liquids, found that the swelling power bears an intimate relation to the specific inductive capacity of the medium.

In 1903 Perrin[18] raised the question whether the property of giving colloidal solutions could not be connected with a high dielectric constant of the dispersion medium. Indeed at that time the only "solvents" known were water, sulfuric acid, glycerin, methyl and ethyl alcohols, and acetone. Perrin was led to advance, as probably correct, the view that "Ionizing liquids give colloidal solutions," because, as he had just shown, they give a powerful charge by contact to the substance immersed in them, and the electric charge of the granule is one of the conditions which permits it to continue in suspension.

This hypothesis was, moreover, fruitful. It induced Svedberg[19] to try to form his colloidal dispersions in media having low specific inductive capacity, and, as this was successful, he was led to work out a novel method of preparation.

P. P. von Weimarn,[20] in papers prepared between 1905 and 1908, said, in opposition to Perrin, that in obtaining colloidal solutions, one of the most important factors is to choose a dispersion medium which has a slight dissociative power; for there is a relation between the power to dissociate and the power to dissolve. Von Weimarn in thus choosing his dispersion media, obtained a large number of new sols, among others of the salts of alkalis and alkaline earths; he thus at this time contributed the important idea that any substance, under proper conditions, can be brought into the colloidal state. (See page 27.)

When a colloidal solution is produced by simple solution of one substance in another, the specific inductive capacity of the solvent may also be the cause of colloidal dispersion. P. Walden[21] found that tetraisoamylammonium iodide dissolves in *ionized condition* in nitrobenzene (s.i.c. = 35), in *molecular condition* in glacial acetic acid and in chloroform (s.i.c. = 6 and 5), but on the other hand it dissolves in *colloidal condition* in benzene and in carbon tetrachloride (s.i.c. = 2.5).

The importance of the specific inductive capacity in the formation of colloidal systems is thus brought out in certain instances.

Let us consider more closely the question of the stability of colloidal systems. It is known that their stability *also* depends on the charge of the dispersed phase. The charge of a micell has, in each case, a variety of factors which usually vary simultaneously but at different rates. Among such factors are, for example: ionization of molecules fixed by the micell; spontaneous ionization of ampholytes; part of the charge is produced by contact potential. These ionization factors and the contact potential are influenced by the specific inductive capacity of the dispersion medium.

The specific inductive capacity of the dispersion medium may be modified by the addition of liquids having very different s.i.c. "Slightly solvated" solutions in particular are sensitive to variations of micellular charge, and therefore to variations in the specific inductive capacity of the "solvent," the lowering of which is generally followed by coagulation.

Wo. Ostwald[22] thus explains the coagulation of silver hydrosol by propyl alcohol.

We have carried out[23] several series of experiments on coagulation, using alcosols because they are readily miscible with substances of low specific inductive capacity. To alcosols of HgS, CuS, and Pt we added variable amounts of liquids whose s.i.c. varied from 1.8 to 81. The addition of substances having a specific inductive capacity higher than that of the "solvent" has no coagulating effect, whereas those having a lower s.i.c. produced coagulation, generally in proportion to the smallness of their specific inductive capacity.

This influence of the specific inductive capacity of the dispersion medium on the charge of micells of dyes has been studied by Keller,[24] who believes that the charge and even the sign of the charge of the dyes studied, depend on the p_H and on the specific inductive capacity of the "solvent"; these two causes may reinforce or may balance each other, or one may gain ascendency over the other if there is an antagonism. Arguing from Coehn's law, Keller thus explains the change of sign in the charge of certain dyes when they pass from an aqueous to an alcoholic dispersion medium.

R. Fürth and R. Keller[25] have called attention to the relatively high specific inductive capacity of human serum (85) and compared this fact with its chemical activity. Continuing their investigations on the relation between the specific inductive capacity and certain biological phenomena, they added ethyl alcohol to serum and found that small amounts of alcohol, corresponding to those having a physiological action, cause a surprising increase in its specific inductive capacity (92) as well as in its other physico-chemical properties. They explain these phenomena on Debye's theory of dipoles.

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The Osmotic Pressure of Colloidal Solutions

By Dr. J. Duclaux, Pasteur Institute, Paris *

On looking over the monographs and books devoted to the study of colloids, it is seen that few of their authors have a very clear idea as to the rôle and the importance of the osmotic pressure of colloidal solutions. Several indeed, as I shall show by giving an example, do not seem to notice that within the distance of a few pages they give contradictory and irreconcilable views as to the definition and height of the osmotic pressure. Others, probably because they have not been able to form a clear idea of it, say nothing about it; and we reach the astonishing conclusion that the study of osmotic pressure, which is above all the most important factor in the study of hydrosols, is the one which occupies a place of minor importance in classical works and original articles.

Colloid theories, as is well known, fall into two distinct groups: physical theories and electro-chemical theories. These theories are not in accord insofar as osmotic pressure is concerned.

As for the physical theories, the particle or micell of each hydrosol behaves as a unit so far as concerns the osmotic pressure. Every particle, no matter what its nature, exerts the same osmotic pressure if equal numbers are present, and this pressure, for dilute solutions, is proportional to the number of particles per unit volume. From this it follows that the value of the osmotic pressure of a sol gives directly the number of particles per unit volume, and consequently may serve to determine the molecular weight of the substance forming the sol. This recalls the conception of Einstein and of Smoluchowski which, because of Perrin's experiments, many chemists regard as definitely proven, notwithstanding the fact that on the contrary, it raises insurmountable difficulties and should be rejected.

As for the electrochemical theories, on the other hand, the micell is an *ionized* molecule, in all respects similar to a salt molecule; it exercises an osmotic pressure essentially dependent upon the number (sometimes very large) of ions to which it gives rise. The osmotic pressure of a sol is proportional (subject to certain limitations which will appear below) to the product of the number of micells per unit volume by the number of ions of each micell. This number being generally unknown, it follows that the osmotic pressure of a sol will not, of itself alone, give the number of micells per unit volume, nor as a consequence the molecular weight of the substance forming the sol.

I insist that these two conceptions are irreconcilable and that no agreement between them is possible. The one extends to colloids the theory of electrolytes; the other, the theory of non-electrolytes. It is obvious that, from an experimental point of view, since certain electrolytes show very slight ionization, the two theories give concordant results for these electrolytes: but that does not disprove the fundamental difference between the two.

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* Translated by Jerome Alexander.

It is curious to note, as I have said, that this incompatibility between the two theories is not more generally commented on, and that they are even in the selfsame work applied successively without explanation. Thus we find in the book of T. Svedberg,[1] an exposition of the physical theory, with a calculation of the osmotic pressure according to Einstein, which does not question the validity of this theory. However, further on (pp. 202-203) we find given the calculations of Donnan, based on the electrochemical theory according to which the osmotic pressure is proportional, not to the number of molecules, but to the number of ions: which is in conflict with the Einstein-Smoluchowski-Perrin theory and leads to very different values for the osmotic pressure, the coefficient of diffusion, and the Brownian motion.

It is true that Svedberg does not speak of ions of the micell in the same sense in which they are taken in the electrochemical theory, but of the *diffusible ions* of the micell; meaning by that the ions of substances fixed (mainly by adsorption) on the micells. But the distinction is of no importance in the present case. If we consider one of the particles used to study the Brownian motion, to which we may suppose Einstein's equation to apply, we may always attach to it an electrolyte giving *diffusible ions; one single* ion like this will give with Donnan's formula twice the value as with Einstein's formula. So that we can reconcile the contradiction only by postulating that the particles studied by Perrin carry not one single diffusible ion (all the more so if a larger number) while the particles of hydrosols which are a thousand times smaller may carry several. This is obviously not admissible, and the two modes of calculation are really irreconcilable. One or the other must be renounced.

The physical theory is simpler, and it is to this simplicity that it owes its rather general acceptation. Unfortunately it cannot be sustained and ought to be abandoned in the usual case of sols formed in an ionizing medium. Although it is founded on the apparently sound basis of the theorem of the equipartition of energy between the degrees of freedom of a system, it leads to inaccurate results, since the conditions under which this theorem is applicable are not fulfilled.

Incomplete though it may still be, the electrochemical theory is indisputably superior. The general outlines of this theory have long ago been pointed out,[1a] but it is only within the last few years that it began to attract attention.[2] Its importance is not, of course, limited to the study of osmotic pressure; indeed the various attempts [3] to extend to colloids the law of proportion and the formulæ of the reactions of ordinary chemistry are in fact merely an application of this theory. For a discussion of this application and others similar, I refer to the papers already cited, limiting myself here to the development with reference to osmotic pressure, and to the demonstration of the facility with which the theory explains otherwise inexplicable experimental facts.

Electrochemical Micellular Theory

The point of view we take is the following: A colloidal micell is a large molecule having all the properties of ordinary salt molecules. More specifically, if the dispersion medium is an ionizing one, the micell is ionized and as a result the hydrosol is a conductor of electricity.[4] The ionization of the micell, like that of the molecule, is more or less complete, depending on its chemical nature and the concentration; the conductivity of the hydrosol, like that of saline solutions, depends on the degree of ionization of the micells, on their number, and on their speed of migration.

In an ionized salt molecule we distinguish ions of two signs. Similarly with micells we have ions with two signs. One of these ions is very large; it is the *granule* or nucleus of the micell which is in general the only visible part of the micell, and then only with the ultramicroscope. The other ions with contrary sign, are the *exterior ions* of the micell: they may also be colloidal, that is to say of large size, but in the immense majority of cases they are ordinary ions, metals or metalloids, or simple radicals such as SO_4, NO_3, etc. For example in colloidal ferric hydrate prepared by the hydrolysis of ferric chloride, the exterior ions are Cl ions, while the granule is a complex of iron, oxygen and water. The electrochemical formula of the micell is

$$[n\,Fe_2(OH)_6, Fe_2]Cl_6$$

the part between the brackets representing the granule.* The electric charge of this granule is of course equal in absolute value to the total charge of the exterior ions, since the total charge of the ensemble is zero.

This electrochemical formula, as may be seen, is the analog of the electrochemical formula of crystalloid salts, and should be interpreted in like manner. Between the two cases there is, however, a very marked difference, to which I have already drawn attention,[5] and whose consequences we will examine more in detail. This difference arises from the fact that the dimensions of an ordinary molecule and those of a micell are not of the same order.

In crystalloid solutions the ions of the two signs are distributed uniformly throughout the mass of the solvent, that is to say that equal volumes of this solvent enclose the same number of the two ions (unless of course the dilution is too great). *The case is not the same with hydrosols:* there the exterior ions, by electrostatic attraction, are concentrated about the granule.

Consider an isolated granule in a liquid medium. This granule carries an electric charge of several units and consequently forms a center of attraction. If there were no thermal molecular agitation, all the exterior ions would attach themselves to the surface of the granules. As a result of this agitation they fly away from this surface and occupy a mean position in which the attraction of the nucleus is balanced by the mutual repulsions of the ions and by what we may somewhat improperly term the *force of diffusion* resulting from the molecular movements.

In this state of equilibrium, there exists a certain stable distribution of ions about the granule. It is impossible to calculate this distribution exactly, nor what we may call the *average distance* of the ions from the granule, for we do not know the form of the granule nor the distribution of the electric charges which it carries. But in the absence of exact calculation, we can quite easily determine the order of magnitude of this average distance, and we will see that this result suffices to give us the key to a certain number of phenomena experience has revealed, for which no other probable explanation can be given.

For the purposes of calculation, we will suppose the granule to be spherical. Because of its symmetry the distribution of ions about the granule will also be spherical. These ions are under the influence of forces tending to make them fly apart, and other forces tending to draw them together; the former are thermal agitation and the mutual repulsion of ions, the latter are the electrostatic attraction of the granule and cohesion. We may at once eliminate the latter which exerts an influence in determining the number of exterior ions of the micell, without affecting their distribution.

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* In passing I would observe that the electrochemical formula permits a prognostication of its reactions, qualitatively and quantitatively; it is indispensable for the study of micells, just as the chemical formula is indispensable for the study of molecules.

The mutual repulsions of the ions can evidently only increase their average distance from the granule; in order to simplify the calculation, I shall take no account of this, so that the figures we obtain will represent a minimum. There remain as factors controlling distribution the attraction of the granule and the Brownian motion. The problem may be treated along the lines of the distribution of particles in order of height in the experiments of J. Perrin; we will assume that each spherical layer of ions is in equilibrium under the action of two opposing forces, the attraction of the granule and the osmotic pressure[*] of the atmosphere of ions.[†]

If $e =$ the elementary electric charge
$P =$ the number of exterior ions of valence p
$N =$ the Avogadro number,
then $Ppe =$ the charge of the granule.

Let $c =$ the concentration (number per unit volume) of ions at a distance r from the center of the granule. The number of ions included in a section of surface ds having a height of dr is

$$c\,ds\,dr$$

If K is the specific inductive capacity of the solvent, the electrostatic attraction of the granule on these ions will be

$$\frac{Ppe^2\,c\,ds\,dr}{Kr^2}$$

The molecular concentration of ions is $\frac{c}{N}$, and consequently the osmotic pressure of the section considered is

$$RT\,\frac{c}{N}\,ds$$

and the resultant of the osmotic pressures on the two faces of the section is

$$\frac{RT}{N}\,\frac{dc}{dr}\,ds\,dr$$

so that the equation of equilibrium is

$$\frac{Ppe^2c}{Kr^2} = \frac{RT}{N}\,\frac{dc}{dr}$$

which on integration gives

$$c = Ae^{\frac{Ppe^2N}{KRT}\,\frac{1}{r}}$$

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[*] As in the theory of J. Perrin, the osmotic pressure is here merely a mathematical fiction representing the coefficient of diffusion. I will in another place publish the justification of this method of calculation, which serves, as I again say, to give but a general orientation.

[†] The idea that neighboring micells may exchange ions, was advanced by Cotton and Mouton ("Les Ultramicroscopes," p. 164, Paris, 1906). I took this up again in 1909, showing the importance of the mean distribution (*J. Chim. Phys.*, 7, 417). This idea should be extended further and almost everywhere replace the old notion of the double layer which gives an incorrect picture of the facts.

From this formula it is obvious that in a general way the concentration of ions is a maximum in the neighborhood of the granule and diminishes in proportion as the distance from the granule increases, tending towards a constant value A.

We may introduce into this equation the respective numerical values at ordinary temperature:

$$
\begin{aligned}
e &= 4.8 \times 10^{-10} \\
N &= 6 \times 10^{23} \\
K &= 80 \text{ (for water)} \\
RT &= 2.38 \times 10^{10}
\end{aligned}
$$

Making the calculation, the formula becomes

$$c = Ae^{\frac{7.2Pp}{10^8 r}} = A \,.\, 10^{\frac{3Pp}{10^8 r}}$$

Now take the special case of a granule carrying 12 monovalent ions, and having a radius of 2 μμ or 2×10^{-7} cm.; on calculating with these figures the concentration of ions at the surface and at various distances from the surface of the granule, we find the following (A being a constant, depending on the total number of ions):

At the surface	63 A
At a distance of 1 μμ	16 A
" " " " 2	8 A
" " " " 4	4 A
" " " " 8	2.3 A
" " " " 30	1.2 A

It is evident that the concentration diminishes rapidly, but it is nevertheless still considerable at a distance from the granule of 4 times its radius. This number is a minimum because, as we have seen, it is obtained by neglecting the repulsions of the exterior ions which drive them still further from the granule.

In every way it is seen that the conception of the double layer does not at all correspond with the actuality, except in the exceptional case where the forces of cohesion are so large that there are no exterior ions, and where as a consequence the conductivity of the hydrosol is zero. For almost every one of the hydrosols, we are going to consider the micell as being formed of a granule surrounded by an atmosphere of ions extending a certain distance, which may even be considerable as compared with the dimensions of the granule.*

Let us now try to calculate the osmotic pressure exerted by a hydrosol containing these micells. To do this we will introduce the idea of *osmotic valence* which may be defined as follows: the *osmotic* valence of a micell is the number of independent particles which exert the same pressure as that micell. According to the physical theory of Einstein-Smoluchowski-Perrin, the osmotic valence will always be equal to unity; according to the electrochemical theory it is greater than unity.

To simplify the argument, we will start with this principle, expressed in the formula of Van't Hoff, that the osmotic pressure of a solution is equal to the pressure the dissolved substance would have if it were in the gaseous state in the absence of the solvent. Imagine then a very dilute hydrosol, containing micells so far apart that their atmospheres do not touch. Each micell will always contain the same granule and the same ions united by their mutual attractions. It is obvious that under these conditions the osmotic valence of the micell is equal to unity. This is, theoretically, necessarily so, and it is also proven by experiment: the instant that a micell remains intact, its internal movements have nothing to do with the osmotic pressure that it exerts, just as the pressure exerted by a gas is independent of the internal movements of the molecule or the atoms so long as the molecule remains intact, that is to say as long as there is no dissociation. The micell we are now considering is analogous to a non-dissociated molecule.

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* This constitution of the micell has several consequences. One in particular concerns viscosity. If an ionized granule, when displaced, drags along its ions, it is evident that the viscosity of a hydrosol will be greater than if its ionization is zero.

Imagine now that the micellular atmospheres mutually interpenetrate each other, either because of the concentration, or for any other reason. There will then be ions which freely circulate throughout the entire mass of the liquid, as is the case with ordinary electrolytes; and as in this case too, each ion acting independently, a micell giving n free ions will have an osmotic valence of $(n + 1)$—unity representing the part of the granule.

It is evident that the distinction between the case of micells and that of molecules is, that with ordinary electrolytes, the ions can exist in but two states—free or combined; in the first instance the molecule is ionized, in the latter it is not. On the other hand with micells the ions may exist in three states: they may be completely retained (non-ionized micell); they may be separated from the nucleus but retained in its neighborhood, or finally they may be completely free. We might compare the two cases with those found in astronomy: the ordinary molecule is a sun all of whose satellites have hyperbolic orbits, while those of the micell have elliptical orbits and hyperbolic orbits too.

Let us now consider the cases actually found in practice. Everything depends on the diameter of the ionic atmosphere of the micell. Now, to express the concentration c of ions at a distance r from the center of the granule, we have found the formula

$$c = A \, . \, 10^{\frac{3Pp}{10^8 r}}$$

As a first numerical example we have taken a granule having a radius of 2 μμ carrying 12 charges, and in this case the concentration of the ions was considerable at a distance from the nucleus equal to 8 times its diameter. This indicates that the atmospheres of these micells interpenetrate each other even when the total volume of the granules is less than one-thousandth that of the hydrosol; that is, for a diluted solution whose osmotic pressure is slight. It will be all the more the case with more concentrated solutions; therefore with micells of this nature the osmotic valence is always greater than 1.

Imagine now a micell of the same substance, but having a diameter ten times as great, and which for the purpose of fair comparison, we will suppose has a charge 100 times greater, that is, having the same superficial density as in the first example. The variations of the concentration of ions in relation to the distance from the surface of the granule will then be the following:

At the surface	1000 A
At a distance of 1	135 A
2	23 A
4	1 A
8	0.007 A
30	0.00002 A

the letter A designating, as in the first example, a constant whose value is of no importance. As may be seen, in this case the concentration of ions becomes practically zero at a distance from the center of the granule equal to its own diameter. With an equal concentration by weight, there will therefore be a much smaller number of free ions than in the case of the first hydrosol. It may easily be shown that the phenomenon is a general one, and that the larger the micell grows, the smaller becomes its osmotic valence with respect to its mass, and perhaps also in absolute value.

The preceding calculation is not rigorous enough to prove it, but it would seem that at the extreme we would find that the physical theory and the Einstein-Smoluchowski method of calculation is applicable only to very large, slightly ionized, and quite isolated micells, like those studied by J. Perrin. In any event this method of calculation is certainly, as may well be imagined, nearer to the truth (even though it is based on incorrect hypotheses) in the case of suspensions of this nature rather than with true hydrosols.

Another very interesting case, which will give us a very simple explanation of phenomena long known, is that in which the exterior ions of the micell are polyvalent ions. Taking the first example again, imagine that the granule whose radius is 2 μμ, instead of having 12 monovalent ions, has 3 tetravalent ions. The distribution will be as follows:

At the surface	32 A
At a distance of 1μμ	0.13 A
2	0.008 A
4	0.0005 A
8	0.00013 A
30	0.000006 A

that is, the ions will be concentrated in the immediate neighborhood of the granule. Here too it may be shown that the phenomenon is a general one; unless it be of very small diameter, a micell with polyvalent ions will not give free ions, or at least will give a much smaller number of them than a micell with monovalent ions. As a consequence the substitution of polyvalent ions for monovalent ions greatly diminishes the extent of the ionization, and therefore the osmotic pressure and the stability. This conclusion checks with experience, and the theory gives here a simple explanation to what is known as Whetham's law.

Insofar as the electrochemical theory in general is concerned, I am satisfied to rest with these few indications. I am, however, going to examine more in detail two rather well known special cases, and show how the application of the same principles explains the experimentally discovered facts, for which other theories furnish no satisfactory explanation.

Osmotic Pressure of Congo Red

Congo red is a dye whose formula is $C_{32}H_{22}N_6S_2O_6Na_2$; if its molecule is simple, its molecular weight is 696. The osmotic pressure of its solutions have been measured by various experimenters,[7] and their results are concordant: it is within a few per cent of that of a non-ionized substance having a molecular weight of 696. Congo red therefore *apparently* behaves as a non-electrolyte, non-dissociated and non-associated. But it does not follow from this, as has erroneously been claimed,[8] that its molecular weight actually is 696. In the first place if that were so, it would be incomprehensible why it does not diffuse through membranes; furthermore it certainly is dissociated, since according to Donnan and Harris its molecular conductivity is of the same order of magnitude as that of sodium chloride. The hypothesis that the molecule is simple and non-dissociated, though it explains the osmotic pressure, is altogether irreconcilable with the other properties of congo red.

In an effort to resolve this contradiction (whose solution is at once given by the electrochemical theory), Donnan advanced two new hypotheses, which as he himself recognized, do not agree with the facts. One is that the congo red molecule is a polymer $(N_2R)_n$ dissociated into $(NaR)_n$ and Na_n; and this indeed gives the osmotic pressure observed, but leads to too small a conductivity. The other hypothesis is that the molecule is simple and dissociated into Na and R; this is satisfactory so far as concerns the conductivity, but not in respect to the osmotic pressure (loc. cit. 1567-1568), so that finally Donnan attributes the anomaly to the existence of a *membrane equilibrium.* Without questioning here the existence of such equilibria and their possible rôle in other phenomena, it must however be pointed out that they certainly do not intervene in the present instance; in fact, as Donnan himself has remarked, the value of the osmotic pressure is thermodynamically connected with the vapor tension of the solvent, over the diminution of which the properties of the membrane evidently exert no influence. The numerical relations between the composition, the conductivity, and the osmotic pressure of congo red are intrinsic relations, entirely independent of the nature of the receptacle which contains this solution, and therefore theory should explain matters without considering the properties of the receptacle, which is but a measuring apparatus.

These relations may be explained in the most simple fashion by the electrochemical theory. It seems that Donnan thought of this, and the reasons that he renounced it are not clear. In reality the micells of congo red have the formula $(Na_2R)_n$ and are dissociated into Na and R, the latter being the granule while the Na ions are the exterior ions. As ultrafiltration shows, these micells are very small: we have then a condition where a large number of exterior ions are free. Taking up again the example of Donnan, a 1% solution of congo red exercises at a temperature of 17° an osmotic pressure of 260 mm., which is very close to the theoretical figure, and its conductivity, based on a molecular weight of 696 is 126 (NaCl = 116).

Assume that, in agreement with theory, of the $2n$ ions $2p$ are free. As a very simple calculation will show the osmotic pressure of a 1% solution will be

$$260\,\frac{2p+1}{n}$$

Experiment gives 262, which shows that $\frac{2p+1}{n}$ is nearly equal to 1, that is, about half of the ions are free. If we suppose that the velocity of transport of the granule is the same as that of the Cl ion, it follows that the conductivity of a congo red solution equals that of an NaCl solution having the same number of Na ions; or, if you wish, to that of a solution of NaCl totally dissociated, having the same sodium content. The molecular conductivity of 1% congo red solution should then be equal to the molecular conductivity limit of NaCl. Now Donnan's experiments give 117 for congo red and 116 for NaCl; the agreement is perfect (which must not be always expected) and we may say that the explanation of the properties of congo red raises no difficulty. It is true we have not the value of n; but it suffices here to know that it is several times unity, which other properties of congo red show beyond doubt.

Osmotic Pressure of Gelatin

The measurements of J. Loeb [9] on gelatin furnish another example of the application of the micellular theory. Here again other theories fail or lead to hypotheses very difficult to justify.

J. Loeb observes that at equal pH, solutions of barium gelatinate have a conductivity equal to that of sodium gelatinate, although their osmotic pressure is twice as low. Likewise gelatin sulphate, with equal pH and conductivity, has an osmotic pressure almost three times * lower than the chloride.

He believes that this anomaly is to be explained by an electrostatic action of the ions on the density of the double layer. But in reality this anomaly has no existence: the phenomena are exactly what they should be according to the electrochemical theory. Let (GBa) and (GNa_2) represent the micells of the gelatinates: the fact that, at the same pH they give to the solution the same conductivity, shows that the number $2p$ of the Na ions is double p of the Ba ions of double charge (assuming for the sake of simplicity that their speed of transport is the same). Whence, at equal concentrations, the theory indicates that the osmotic pressures should be

$$(2p + 1)\,RT \text{ for the Na salt}$$
$$(p + 1)\,RT \text{ for the Ba salt}$$

The ratio of these two numbers is close to 2, as experiment indicates, since p is large, that is, since the gelatinate molecule carries a large number of ions: which is certain from other evidence, because of the size of the micell which contains a large number of ions. Thus here too micellular theory promptly explains the observed facts.

Résumé

The micellular or electrochemical theory of colloidal solutions compares the particle or micell of the colloid to a big ionized molecule. In this micell we distinguish the granule or nucleus, of relatively large size, and the exterior ions. The granule carries an electrical charge of ionic origin and it is neutralized by the exterior ions like an ionized molecule of the ordinary type.

Because of the size of the granule, the exterior ions concentrate in its neighborhood, but without forming a double layer: they move out to a certain mean distance. Some are entirely free: others are retained by the granule. In general the proportion of the number of free ions to the total number, that is to say the ionization of the micell, diminishes proportionately as the micell is larger and the valence of the exterior ions higher. It depends in a complex manner on the concentration, and it may be that it is stronger with concentrated solutions than with dilute solutions.

From the point of view of osmotic pressure, the micell is equivalent not to a single particle, but to a certain number of particles. This number is the osmotic valence of the micell; it is always larger than unity, but under certain circumstances it may practically equal 1.

Since it was advanced in 1907 and 1909, the micellular theory has been the one which, despite its inevitable imperfections, explains in satisfactory

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* According to the figure accompanying the text, it seems that this should be *two times* instead of *three times*.

fashion the experimental results on osmotic pressure and conductivity of hydrosols, that is, their two fundamental properties. This is particularly shown by two examples, congo red and gelatin, studied experimentally by Donnan and by Loeb.

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Evidence against the views advanced by Dr. Duclaux is to be found in many papers of this volume, *e.g.,* those of W. Kopaczewski, L. Michaelis, Sir W. B. Hardy, I. Langmuir, H. J. Weiser, R. A. Millikan. The "colloidal electrolytes" of McBain, the "giant ions" of Michaelis, and the colloidal oil droplets of Millikan have no uniformity in size or composition, and their charges are various and varying. Thus Millikan reports oil droplets having from 1 to 136 electrons. Any general theoretical treatment must consider aerosols and sols in non-ionizing media. Since momentum (MV) and kinetic energy ($\frac{1}{2}MV^2$) are both functions of velocity, and since mass and velocity vary at different rates (see p. 14 *et seq.*), the assumption that every particle exerts the same osmotic pressure seems unfounded.

The main differences between the physical and chemical theories are in terminology and point of view, rather than point of fact. The chemist strives to pin everything to the atom or molecule, while the physicist deals with the physical unit or particle, which only in the limiting case is a molecule. (See *e.g.,* W. D. Bancroft, Third Colloid Symposium Monograph, Chem. Catalog Co., 1925.) J. A.

The Effects of Molecular Dissymmetry on Properties of Matter

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The kinetic theory of gases during the last century led to extremely valuable conceptions and even quantitative laws, notwithstanding the fact that in the development of the theory, it had been necessary to make many simplifying assumptions which frequently were not actually correct. For example, in most derivations it was assumed that the molecules were infinitely hard elastic spheres which acted on one another only at the instant of contact. In this way it was possible to account quantitatively with fair accuracy not only for the effects of pressure and temperature on the volume, but for the viscosity, heat conductivity and diffusion of gases, and other phenomena involving the free paths of the molecules. Maxwell, on the other hand, developed a very complete theory based on the assumption that the molecules are point centers of force repelling one another according to the inverse fifth power of the distance between them. This assumption was made not because it was supposed to correspond to the actual forces around molecules, but because it lent itself particularly well to mathematical treatment. The results obtained by Maxwell differed from those based on the assumption of elastic spheres mainly in slight differences in numerical coefficients of the equations obtained. To handle the problem mathematically it was necessary to make assumptions as to the forces between the molecules, but to get most of the essential truths of the kinetic theory it did not much matter exactly what these assumptions were.

To account for the main features of the transition from the gaseous to the liquid state Van der Waals found it necessary to consider attractive forces, but again the particular law of force did not need to be known to obtain this useful result. Sutherland also took into account attractive forces in dealing with the temperature coefficient of the viscosity of gases.

In considering other properties of gases or liquids it may be necessary to analyze the forces around molecules in more detail. For example, Debye[1] showed that the variation of the dielectric constant of a substance with temperature depends on an orientation of the molecules in an electric field, thus indicating that these molecules are electric dipoles.

W. B. Hardy[2] in discussing the interfacial surface tension between fluids said in 1912:

"If the stray field of a molecule . . . be unsymmetrical, the surface layer of fluids and solids, which are close packed states of matter, must differ from the interior mass in the orientation of the axis of the fields with respect to the normal to the surface, and so form a skin on the surface of a pure substance having all the molecules oriented in the same way instead of purely in random ways."

In a later paper[3] he adds:

"The surface film must therefore have a characteristic molecular architecture. . . . When the composite surface is formed its architecture is determined by the interaction of the fields of force of molecules of A and B under the influence of the attraction of B for A."

In connection with a study of chemical reactions at the surfaces of highly heated tungsten and carbon filaments in gases at low pressures (less than 0.1 mm.) I came to the conclusion[4] that adsorbed carbon monoxide must be regarded as oriented on the surface, so that the carbon atoms are attached to the solid while the oxygen atoms form the surface layer.

Shortly thereafter, without at that time knowing of Hardy's work, I saw the application of these ideas to the orientation of molecules at the surfaces of liquids, and was then able to develop a theory of the effect of chemical constitution on the surface tension of pure liquids as well as solutions and oil films on water.[*]

It is the object of the present paper to consider in a general way the causes of molecular orientation and the effects produced by such orientation on surface tension, solubility, vapor pressure, etc. In particular, since the chemist knows a good deal about the shapes of molecules and the stray fields around their different parts, it will be urged that this knowledge be used to correlate, as nearly quantitatively as possible, the various so-called physical properties which depend on these factors. For this purpose it will not be necessary to have knowledge of the exact shapes and fields of forces of the molecules, but, just as in the case of the kinetic theory, considerable progress may be made even by the crudest kinds of assumptions in regard to these factors.

We know that molecules actually exist and must be of the most varied shapes. Let us therefore consider how the various possible shapes of the molecules and the types of force fields must influence the physical properties of substances.

TYPES OF INTERATOMIC AND INTERMOLECULAR FORCES

The chemical properties of matter are primarily dependent on the number of electrons in the atoms and the manner in which these electrons are able to arrange themselves to form the most stable configurations. The electric forces due to charges on the atoms frequently oppose the formation of certain configurations which, except for these charges, might be the most stable. The effect of these two factors in governing chemical action has been discussed at some length by the writer.[†]

The electron configurations existing in the atoms of the inert gases He, Ne, Ar, etc., are the most stable of all. Other atoms, by taking up, or giving up electrons, or by sharing electrons with each other, strive to obtain electron configurations like those of the inert gases. It is mainly as a result of these changes that chemical interaction occurs.

Each of the ions O^{--}, F^-, Na^+, and Mg^{++} contains 10 electrons, the same number as in a neon atom. The reason for the formation of chemical compounds containing these ions is that the electrons can thereby become arranged in the stable configuration characteristic of the neon atom.

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[*] A paper on this work was read before the American Chemical Society in September, 1916, and a two-page abstract was published in *Met. Chem. Eng.*, 15, 468 (1916). Before the full work could be published, two papers by W. D. Harkins appeared in *J. Amer. Chem. Soc.*, 39, 354 and 541 (1917), which dealt in detail with the surface tensions of pure liquids. In the final publication of my results, *J. Amer. Chem. Soc.*, 39, 1848 (1917), the part dealing with pure liquids was therefore omitted.

[†] "Types of Valence," I. Langmuir, *Science*, 54, 59-67 (1921). The recent work of Bohr, which has proved that the electrons in the heavy atoms (such as niton) are arranged in shells according to the scheme 2, 8, 18, 32, 18, 8 instead of the scheme 2, 8, 8, 18, 18, 32 postulated by the writer, requires only a slight and obvious modification of the wording of Postulate I, and does not otherwise affect the validity of the conclusions that were drawn in that paper.

This view, which is largely that of Lewis and Kossel, and is now generally accepted, may serve as a basis for a classification of intermolecular forces. There are three main types of molecules to consider: * (1) Non-polar, (2) Polar, and (3) Ionic, as follows:

1. Non-polar.

The neon atom, or methane molecule, may be taken as the most extreme example. The center of gravity of the electrons of the molecule coincides with that of the positive charges of the nuclei, so that there is no dipole moment. In general, however, the atom or molecule may behave as an electric quadrupole or system or even higher symmetry. Debye has shown that quadrupole molecules † attract one another, when at a considerable distance, with a force which varies inversely with the ninth power of the distances. This result is obtained by considering the deformation of each of two molecules in the electric field of the other. Under the influence of an electric field the electrons become displaced with respect to the nucleus by an amount which may be estimated from the dielectric constant, and thus the molecule becomes polar to a degree which depends on the proximity of other molecules. If the molecule is more symmetrical than a quadrupole (as neon probably is), the force will vary inversely with a power of the distance which may be much greater than the 9th.

In general, non-polar molecules do not become oriented in weak electric fields, but when the field becomes very strong, the dipole moment, which may differ for different orientations of the molecule, may cause orientation. However, thermal agitation will nearly always make such orientation negligible for molecules of this type.

2. Polar.

The molecules of hydrochloric acid gas and water vapor are extreme examples. The center of gravity of all the electrons of the molecule does not coincide with that of the positive charges, so that the molecule acts as an electric dipole. If the separation of the centers of gravity of the electric charges is comparable with the distance between the atoms in a molecule the electric forces are much more intense than in the case of non-polar molecules. The attractive force due to deformation is thus greater than for non-polar molecules. The polar molecules become oriented in an electric field in so far as the thermal agitation will permit. Thus the dielectric constant, or rather that part of it which is due to orientation, varies inversely proportional to the absolute temperature.[5] Such orientation of the polar molecules in the field of neighboring molecules, if it occurs to any large degree, causes a very great increase in attractive force between molecules. The amount of orientation increases rapidly as the molecules are brought closer together, and also increases slowly as the temperature is lowered. The force of attraction between two dipole molecules which are oriented in each other's fields is $6e^2\delta^2/r^4$ where e is the charge and δ the displacement of the dipole ($e\delta =$ the

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* P. Debye, *Phys. Zeit.*, 21, 178 (1920), has made this classification based on the degree of symmetry of the distribution of electrons within atoms.

† The word molecule will be taken to include atoms in those cases where the atoms act as individuals, as, for example, in gaseous or liquid neon.

electric moment) and r is the distance between the molecules. The force due to orientation thus varies inversely with the fourth power of the distance.

3. Ionic.

Electrolytic ions such as Na^+, SO_4^{--}, etc., are familiar examples. Gaseous ions must also be included in this group. The molecule, which in this case is an ion, has an unequal number of electrons and protons, or, in other words, the number of electrons is not equal to the positive charges of the nuclei. The electric field around such ions is in general very much greater than around polar and non-polar molecules, and falls off still more slowly as the distance increases. The force between two ions in free space varies inversely as the square of the distance between the ions. But in presence of other molecules, and particularly in presence of other ions, the deformation of the non-polar molecules, the orientation of the polar molecules, and the concentration differences among the ions all tend to decrease the forces between ions. The increased concentration of positive ions around negative ions and vice versa causes the force between two given ions to decrease with increasing distance more rapidly than according to the inverse square law. Debye and Hückel [6] have recently been able to develop a mathematical theory of these effects which has cleared up at one stroke most of the perplexing problems involved in the theory of electrolytic dissociation.

Attractive Forces.

From this analysis we see that there are three fundamental factors that cause attractions between molecules:

a. Deformation
b. Orientation
c. Segregation

Debye has shown that two uncharged molecules, each consisting of a *rigid* structure of positive and negative particles, would on the average exert no force on one another if all orientations of the molecules are equally probable. But, since all substances have dielectric constants greater than unity, the particles must become deformed when they get into each other's fields. This deformation is always such as to cause an attraction between the molecules.

In general, there will also be a tendency for molecules to be oriented when they approach one another sufficiently closely. This orientation always increases the attractive force.

Debye has also pointed out that if, around a given ion in an electrolyte, there were no concentration of ions of opposite sign, there would be no resulting attraction between an ion and its neighbors. But since there is in fact around any ion an increased concentration of ions of opposite sign, there is a resulting attractive force which opposes the osmotic pressure of the ions, due to their thermal agitation. It is this effect which we have denoted by the term *Segregation*. It may occur not only with ions, but also with dipole molecules such as those of water. By the segregation of dipole molecules and their orientation about a given molecule or ion electric forces may be transmitted through distances larger than would otherwise be possible.

Repulsive Forces.

Of course the attractive forces in matter must be balanced by equal repulsive forces. Very little has been definitely known about these forces except that they vary inversely with some very high power of the distance between molecules. In the past in the kinetic theory it has been usual to take into account these repulsive forces merely by assuming that the molecules behave like infinitely hard elastic spheres which is equivalent to assuming that the force varies inversely with an infinite power of the distance.

In order to account for the compressibility of solids Born and Landé[7] have shown that definite exponents for the repulsive force must be assumed. Thus in the case of halide salts of the alkalis such as NaCl, KI, etc., he showed that the compressibility of the solid salts indicated that the repulsive force varied inversely as the 10th power of the distance between the ions, while the attractive force varied inversely as the square of the distance in accord with Coulomb's Law. Born[7a] also attempted to show that the inverse 10th power law for repulsion could be *deduced* by assuming that the electrons in the ions were arranged with cubic symmetry as at the corners of a cube. This attempt, however, must be regarded as a failure for two reasons. 1st. The method of mathematical expansion used is not legitimate when applied to distances as short as those between ions in salts, and 2nd, Born assumed that the cubical ions were all oriented so that their edges are parallel. This kind of orientation would be unstable under the forces assumed. If the atoms should become oriented in response to the forces acting, the repulsive force would disappear and would be replaced by an attractive force which would act in addition to the force between the ionic charges.

Such orientation of ions as Born assumes may very possibly exist in solid crystals from causes which he does not discuss, but this orientation cannot be the cause of the repulsive forces which determine the compressibility, since the elimination of the orientation by melting the salt does not greatly alter the density or the compressibility, whereas by the reasoning of Born's theory the repulsive forces, being then unbalanced, should cause a complete collapse of the structure.

Thus we cannot regard Born's theory as one that throws any light on the cause of the repulsive forces.

Debye,[8] however, has recently developed a theory which seems to indicate the nature of the repulsive forces. It depends essentially on the orbital motions of the electrons within the atoms in accord with Bohr's theory, whereas Born in his calculations had assumed that the electrons acted as if stationary. Debye assumes that the conditions imposed by the quantum theory determine the size of the electron orbits and the frequency of rotation in these orbits. Thus the electric field around an atom or molecule is not a static field but is a pulsating or partly oscillating field increasing in amplitude of oscillation very rapidly as the surface of the atom is approached. Thus when an electron approaches an atom it acquires in addition to any motion of translation it may have, an oscillatory motion due to the pulsating field. Debye shows that this oscillatory motion tends to be 180° out of phase with the field producing it, and then shows, that because of the non-uniformity of the electric field near an atom, the resulting force will be one of repulsion. This repulsive force may be assumed to exist not only for free electrons but for electrons which themselves are involved in the orbital motions of other atoms.

Thus the repulsive forces between atoms and molecules are due to the perturbations in the electron orbits caused by the motions of the electrons which revolve in orbits in neighboring atoms. The repulsive force does not originate from an atom as a whole, but comes from the close approach of electrons in the two atoms. Thus we should look upon these forces as surface forces and should try to express them as functions of the distances between the surfaces of the atoms (fixed by the outer electron orbits) rather than in terms of the distances between the centers of the atoms.

Forces at the Surfaces of Molecules

In a discussion of the compressibility of metals and its relation to interatomic forces [9] the writer has shown that the range of the attractive forces between the atoms is approximately the same for all metals, although the compressibilities of the metal and the volumes of the atoms vary over wide ranges. Thus although the compressibility of cæsium is 220 times that of tungsten, and the atomic volume is 7.4 times that of tungsten, the range of the attractive force is nearly the same, 0.66×10^{-8} and 0.57×10^{-8} cm. respectively.

Debye [10] in a paper of 1920 in analyzing the causes of attractive forces between non-polar molecules attempts to calculate the force from assumed stationary electron configurations. For this purpose he expressed the electric potential in the neighborhood of a given molecule in terms of an infinite series expanded according to reciprocal powers of the distance r from the center of the molecule. If the molecule is uncharged (*i.e.*, is not ionic) the first term which involves $1/r$ vanishes. If the molecule is non-polar (*i.e.*, has no electric dipole moment) the second term involving $1/r^2$ vanishes. For a non-polar molecule, which is of the type of a quadrupole, the third term is therefore the first term which does not vanish. Debye considers therefore the effects due to this term involving $1/r^3$ and *neglects all subsequent terms in the series*. If, however, the molecule has a higher degree of symmetry than that of a quadrupole (for example a tetrahedron or cube) the third term (which is the only one that Debye considers) should also vanish.

Debye then calculates that the average force which acts on a molecule B when at a distance r from a similar molecule A is given by

$$F = \frac{24\alpha\tau^2}{r^9} \qquad (1)$$

where t is a function only of the "electric moments of inertia" (Σex^2, Σey^2 and Σez^2) determined by the positions of the electrons and nuclei in the molecule. The quantity α measures the deformability or ease of polarization of the molecule in an electric field and can be calculated from the dielectric constant, or better from the molecular refractive index.

Debye then proceeds to test these conclusions by calculating from this equation the coefficient a in the van der Waals' equation.

$$\left(p + \frac{a}{V^2}\right)(V - b) = RT \qquad (2)$$

which measures the attractive forces between molecules. He finds

$$a = \frac{6\pi}{5} \cdot \frac{N^2\alpha\tau^2}{d^5} \qquad (3)$$

where N is the Avogadro constant (6.06×10^{23}) and d is the diameter of the molecule. In deriving this relation Debye assumes that the force between the molecules is given Equation by 1 for all distances from d to ∞. Considering the derivation of Equation (1) it is clear that we have no right to apply it to distances comparable with the diameter of the molecule, for the neglected terms in the expansion on which it is based, should then be as important as the term actually considered. Debye, however, uses Equation 3 to calculate τ from the experimentally determined values of a.

He then compares the values of τ obtained in this way with those calculated by another method from the Sutherland constant c which is determined from the temperature coefficient of the viscosity η of gases by the equation

$$\eta = \frac{\text{const}\,\sqrt{T}}{1 + \frac{C}{T}}$$

The Sutherland constant is a measure of the attractive forces between molecules and thus Debye is able to express it in terms of τ which occurs in Equation 1.

The values of τ calculated by these two independent methods agree very well with one another (average error about 4 per cent) for the gases argon, krypton, xenon, nitrogen, oxygen and ethylene which have molecules of the non-polar type. For hydrogen and helium, however, the errors are about 50 per cent. Debye concludes that this good agreement indicates that "the law of force (Equation 1) and its interpretation correspond completely to reality." Undoubtedly the agreement justifies the use of the inverse 9th power law of attractive force between non-polar molecules and the relation between the attractive forces and the refractive index, but it should not be concluded that this is evidence of the correctness of the relation between τ and the assumed arrangement of electrons (electric moment of inertia).

With a force which varies with the inverse 9th power, the force falls to one-half value for an increase of only 8 per cent in the distance. Thus the cohesive forces corresponding to the van der Waals and Sutherland constants are determined mostly by the forces exerted by the molecules upon one another during the times that their distance apart does not exceed the distance of minimum approach by more than 10 per cent.

When a molecule is as close as this to another the force acting at the near side of the first molecule would be about 10000 times as great as the further side of the molecule. We are then surely not justified in considering that the deformation would be the same as if the molecule were in a uniform field having the intensity of that at the center of the molecule. The fact that Debye does get good agreement must be due to two compensating errors. 1st the field at the near side of the molecule where it alone needs to be considered is much stronger than that calculated by Debye, and 2nd this field acts effectively on only a small part of the molecule and its effect is thus reduced.

Examining Debye's data we find that the values of τ which he finds are quite accurately proportional to the 4th power of the molecular diameter. From this it can be shown that the root-mean square electric field at the surface of the molecule which causes the mutual polarization of the molecules when they are in contact is practically the same for all the substances considered, and has the value of 9.8×10^{8} volts per cm. (for $r = d'$) which is the field that exists at a distance 1.21×10^{-8} cm. from an electron.

Thus we see that the intensities of the fields around different non-polar molecules are practically identical when regarded as surface forces rather than as forces which originate at the center of the molecules.

SURFACE FORCES AS THE CAUSE OF MOLECULAR ORIENTATION

The surface tension γ of a liquid is the free energy per unit area or is that part of the surface energy which can do work. The total energy per unit area γ_0 is given by

$$\gamma_0 = \gamma - T\frac{d\gamma}{dT} \qquad (4)$$

To produce isothermally a new surface of unit area we must expend the work γ, but the total energy increases by more than this, the difference $-T\frac{d\gamma}{dT}$ being derived from heat energy, and thus causing a cooling effect.

In general the temperature coefficient $\frac{d\gamma}{dT}$ is practically constant, and therefore by Eq. (4) γ_0 is constant and equal to the value of γ at $T = O$. From the linear change of γ with temperature it is probable that the variation of γ is a direct result of the thermal agitation of the molecules, and is not due to any change in the structure of the surface. In studying the effects of molecular orientation we must, therefore, consider the total energy γ_0 rather than the free energy.

In the early work on the orientation of the molecules in the surfaces of organic liquids, the writer pointed out that the different portions of the molecules produced their characteristic effects independently of the presence of the other portions of the molecular surface. Thus it was stated:[11]

> "The surface energy of a liquid is not a property of the molecules, but depends only on the *least active portions of the molecules* and on the manner in which these are able to arrange themselves in the surface layer. In liquid hydrocarbons of the paraffin series the molecules arrange themselves so that the methyl groups at the ends of the hydrocarbon chains form the surface layer. The surface layer is thus the same no matter how long the chain may be. As a matter of fact the surface energies of the hydrocarbons from hexane to molten paraffine, have substantially the same surface energy (46-48 ergs per cm.^{2}) although the molecular weights differ very greatly. If we consider the alcohols such as CH_3OH, C_2H_5OH, etc., we find that their *surface energies are practically identical with those of the hydrocarbons.* The reason for this is that the surface layer in both cases consists of CH_3 groups."

We see that this conception of surface forces is in agreement with the conclusions that we have reached by our more general considerations of intermolecular forces. We may, however, use this idea of separate surface energies for different parts of the molecular surface, to explain the orientation of the molecules and many other phenomena observed in liquids.

Let us apply the idea of surface energy to the surface of a molecule in the same manner as we apply it to a large surface of a liquid. As an example we will consider a molecule of palmitic acid, $C_{15}H_{31}COOH$ and calculate the difference in surface energy when the molecule is in various environments. From the density 0.85 and the molecular weight 256 the volume per gram molecule is 301 cm^3 and from the Avogadro number we find the volume per molecule to be 497×10^{-24}cm^3. Because of surface tension forces a molecule of palmitic acid vapor will assume a nearly spherical form in which the carboxyl group is buried as completely as possible within the sphere. Thermal agitation and internal stresses in the molecule will tend to prevent the molecule from being truly spherical, but with a molecule as large as palmitic acid the effect of the surface energy should predominate and make the molecule approximately spherical. Let us estimate the maximum and minimum surfaces which the molecule may possess.

The minimum surface will correspond to the spherical form. The diameter of a sphere having a volume * of 497 A^3 is 9.83 A and its surface is 304 . A^2. The maximum area occurs when the hydrocarbon chain is as nearly straight as possible. The experiments on adsorbed films on water have shown a minimum cross-section of 20 A^2 for the hydrocarbon chain. If we consider the molecule to be a cylinder having this cross-section and having hemispherical ends, we find the diameter to be 5.04 A, the length of the cylindrical part 21.5 A and the total surface 420 . A^2, which is 39 per cent greater than the surface when the molecule is spherical.

The difference in surface (116 . A^2) multiplied by the surface energy of hydrocarbons (50 ergs per cm.^2) gives the energy involved in the transformation between the cylindrical and the spherical form.

Let us then consider whether this energy of $58. \times 10^{-14}$ erg is sufficient to cause the molecule to assume a nearly spherical form.

The ratio P_1/P_2 of the probabilities of the occurrence of any particular configuration of a molecule is given by the modified Boltzmann equation

$$\frac{P_1}{P_2} = \frac{p_1}{p_2} e^{-\frac{\lambda}{KT}} \tag{5}$$

where λ is the energy required to change the molecule from the state 2 to state 1, and p_1 and p_2 are the *a priori* probabilities of the two states, which are largely determined by geometric factors and the definitions of the two states. If we put $\lambda = 58 \times 10^{-14}$, $T = 293$, the exponent is — 14.4 and the exponential factor is thus 6×10^{-7} so that nearly all the molecules must be in a nearly spherical form unless p_1/p_2 has a very large value. If the surface energy λ were zero the ratio p_1/p_2 would measure the relative probabilities of the two configurations. Of course the probability p_2 would be zero if we were to consider only absolutely spherical molecules. We should therefore consider a range for each state, taking, for example, state 2 to be one in which the surface area is not more than 5 per cent greater than that of a perfect sphere, while state 1 is one in which the area is not less than 95 per cent of that of the cylindrical molecule already considered.

If λ were zero, thermal agitation would make the molecules assume the most varied shapes. It seems likely, however, that in most of these configurations there will be a relatively large part of the surface of the hydrocarbon chain exposed, so that p_1 will be larger than p_2. But this difference in probabilities will be a very moderate one, not at all able to compensate for the very small value of the exponential factor in Equation (5) when λ has the value $58. \times 10^{-14}$ erg.

In these calculations we have used the total surface energy γ_0 instead of the free energy. The thermal agitation may tend to oppose the contraction of the surface of a single molecule, but probably to a much smaller extent than in the case of a large surface of many molecules. However, the conclusion that there is ample energy to bring about a nearly spherical form would not be altered if λ were half as great as we found, so that for the present we shall not attempt to draw a distinction between free energy and total energy in applying Equation (5).

If a palmitic acid molecule is surrounded by water, the hydroxyl group is nearly completely surrounded by water molecules, while the hydrocarbon chain will draw itself as nearly as possible into a sphere, since the interfacial surface energy between water and hydrocarbon is about 59 ergs, which is even more than the surface energy of a hydrocarbon (against vapor).

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* For convenience we shall express molecular dimensions in terms of the Angstrom unit 10^{-8} cm.; thus 5 $A^2 = 5 \times 10^{-16}$ cm.^3 and 4 $A^3 = 4 \times 10^{-24}$ cm.^3 [A stands for A.U. J. A.]

Before proceeding with the properties of the palmitic acid molecule let us consider the somewhat simpler problem of a hydrocarbon molecule. To facilitate comparison we will assume that the hydrocarbon molecule has the same volume ($497A^3$) as the palmitic acid molecule. This corresponds approximately to hexadecane $C_{16}H_{34}$. Let us now calculate the energy needed to transfer such a molecule from a hydrocarbon liquid to — 1, the interior of a mass of water; 2. a vapor phase, and 3. an adsorbed film on the surface of the water.

While the hydrocarbon molecule is in a liquid consisting of other (saturated) hydrocarbons its surface energy may be taken to be zero, since there are no interfaces, even if the surrounding hydrocarbon molecules are of different molecular weight. When the molecule is transferred to the interior of a large volume of water the surface energy is $\lambda = s\gamma_0$ where s, the surface of the molecule, is 304 A^2 and the interfacial surface energy $\gamma_0 = 59$ ergs per cm. Hence $\lambda = 179 \times 10^{-14}$ erg. For the formation of a molecule of vapor we have the same value of s but $\gamma_0 = 50$ so that $\lambda = 152 \times 10^{-14}$.

These energies correspond respectively to the heat of solution and the heat of evaporation of the hydrocarbon molecule. Actually the heat of evaporation is about 55 per cent of the value calculated in this way. The agreement as to order of magnitude is satisfactory. The surface energy 50. ergs per cm^2 is that which is measured when a fraction (probably about ⅓) of the surface of the molecules is exposed, while the heat of evaporation corresponds to the whole surface exposed. It is probable that the difference is caused by the more unsymmetrical state of the molecule when only part of its surface is exposed and by the resulting increase in the surface energy or stray field.*

From the fact that λ for the hydrocarbon molecule in water or in the vapor state is so large we may conclude from the Boltzmann equation that the vapor pressure and the solubility are very small in the case of a hydrocarbon with a molecule as large as we are considering (16 carbon atoms). With lower molecular weights the surface area of the molecules becomes less and the volatility and solubility thus increase. The relatively small solubility of even the lower hydrocarbons may be explained in this way.

The energy of transfer of a hydrocarbon molecule to an adsorbed film on water will depend on the configuration and the orientation of the molecule in the surface. Let us consider three possible cases:

a. A spherical molecule half immersed in the water. The energy λ is thus the sum of the energies of the two hemispherical surfaces minus the energy of the water surface which is destroyed by the presence of the hydrocarbon molecule. The cross-section of the molecule through the center is 76 . A^2 while each hemisphere has a surface of 152 . A^2. Taking the total surface energy of water to be 117 ergs per $cm.^2$ we have

$$\begin{aligned}\lambda &= (59 \times 152 + 50 \times 152 - 117 \times 76)\, 10^{-16} \\ &= 77 . \times 10^{-14} \text{ ergs.}\end{aligned}$$

b. A cylindrical molecule, half immersed in the water, oriented with its axis parallel to the water surface. The area of the section parallel to the axis is 128 . A^2 and half the molecular surface is 210 A^2 so that

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* In a paper to be published in the *Journal of Physical Chemistry* this theory of evaporation is developed and discussed in more detail and gives quantitative agreement with the heats of evaporation not only of hydrocarbons, but of alcohols and other substances.

$$\lambda = (59 \times 210 + 50 \times 210 - 117 \times 128)\ 10^{-16}$$
$$= 79. \times 10^{-14} \text{ erg.}$$

c. A cylindrical molecule, half immersed in the water, oriented with its axis perpendicular to the water surface. The cross-section of the molecule parallel to the water surface is 20 . A². Thus we have

$$\lambda = (59 \times 210 + 50 \times 210 - 117 \times 20)\ 10^{-16}$$
$$= 206 . \times 10^{-14}$$

Table I gives a summary of these results to facilitate comparison.

TABLE I

Surface Energy of a Hydrocarbon Molecule $C_{16}H_{34}$ Having a Volume 497. A³

Sphere 9.83 A diameter or Cylinder 5.04 A diameter
304. A² surface 420. A² surface

Location of Molecule	Shape and Orientation of Molecule	Energy in Erg $\times 10^{-14}$
In liquid hydrocarbon	Sphere or Cylinder	0
In water	Sphere	179.
	Cylinder	248.
In vapor	Sphere	152.
	Cylinder	210.
Adsorbed on water (half immersed)	Sphere	77.
	Horizontal cylinder	79.
	Vertical cylinder	206.

Surface energies used in calculations—water vs. vapor 117, water vs. hydrocarbon 59; hydrocarbon vs. vapor 50 ergs per cm. as taken from tables by Harkins et al.

The difference in energy between the spherical and cylindrical form when the molecule is in the vapor phase or the water phase is so great that the molecules will be nearly spherical. But with the molecule in the interface the difference in energy (2×10^{-14}) between the sphere and the horizontal cylinder is so small that it will have little effect in determining the shape, the exponential factor in Equation 5 being only 0.61. Thus the configuration of the molecule will depend almost wholly on the *a priori* probabilities. For reasons already given a nearly spherical form is improbable as compared to an extended or irregular form in which the larger part of the molecule is exposed. These considerations lead us to conclude that a hydrocarbon molecule adsorbed on a water surface will lie flat on the surface when not crowded by other adsorbed molecules.

This conclusion is the same as that reached by the writer from a study[12] of the surface tensions of dilute solutions having non-saturated adsorbed films.

The very high value of λ in the case of the vertical cylinder shows that molecules can be oriented vertically only very rarely. The difference in energy between the horizontal and vertical cylinder (127×10^{-14}) gives, when substituted in Equation (5), an exponential factor of 2×10^{-14}. In this case the *a priori* probabilities of the two orientations are the same so that only one adsorbed molecule out of about 10^{14} will be oriented in a vertical direction.

The energy 79 corresponding to the adsorbed molecule is very much less than the 152 for the vapor or 179 for the water phase. We can thus see that the presence of molecules in the interface is very much more probable than in either the water phase or the vapor. This conclusion is strikingly in accord with the facts.

Hexane vapor coming into contact with water lowers its surface tension very considerably. According to Gibbs' Law this proves that there is an adsorbed film of hexane molecules in the surface having a much higher concentration than that of either the vapor phase or the water phase. With hexane the energy of transfer to the adsorbed film is roughly about $6/16$ths of that for hexadecane but the ratio of this energy to that in the vapor or water phase is about the same for the heavier molecule. As the length of the chain increases the vapor pressure, solubility and amount of substance adsorbed decrease, but the ratio of the amount adsorbed to that in either phase must increase.

We shall see that this is the fundamental cause of the formation of monomolecular films of organic substances on water. The *ratio* between the concentration of the substance in the film and in the water is not greatly altered by the presence of an active group (such as carboxyl) in the molecule. The principal effect of the active group is to increase the solubility of the substance in water and therefore cause a corresponding increase in the amount adsorbed.

The Effect of an Active Group.

When we replace a hydrogen atom in a hydrocarbon by a hydroxyl, carboxyl or similar radical we change the surface energy of a part of the molecule very greatly without having very much effect on the remainder of the molecular surface. From this viewpoint we have at once an explanation of the fact that the introduction of such a radical or active group lowers the vapor pressure and increases the solubility.

Let us now take up again the consideration of the palmitic acid molecule as an example of a molecule having an active group. We shall adopt Adam's terminology and refer to the hydrocarbon portion of the molecule as the tail and to the active group—COOH as the head. Representing the molecule by the usual symbol RX we shall thus let R denote the tail and X the head. For the calculations of the surface energies we shall adopt the following values for the surface energies (ergs per cm.^{2}).

$$\gamma_R = 50. \qquad \gamma_{RW} = 59.$$
$$\gamma_X = 144. \qquad \gamma_{RX} = 20.$$
$$\gamma_W = 117. \qquad \gamma_{XW} = -30.$$

The subscript w refers to water. The surface energies of hydrocarbons and of water, γ_R and γ_W respectively are the values we have already used and are those given by Harkins for the liquids in bulk. The same is true for the interfacial energy γ_{RW}. The value of γ_X has been obtained from a study of heats of evaporation of hydrocarbons and fatty acids while γ_{RX} and γ_{XW} were found from a study of the vapor pressures of binary mixtures by a method which we shall soon describe briefly. The negative value for the surface energy between carboxyl and water which results from these studies is in accord with the very marked increase in the solubility in water caused by the presence of this group.

We have already estimated the surface area of the palmitic acid molecule, but we now need to know the surface of the carboxyl group. From a comparison of the volumes of the molecules of the lower fatty acids we may estimate the surface to be 45 . A^2 which is the value that was assumed in obtaining the values of γ_X, γ_{XR} and γ_{XW}.

Table II gives the dimensions of palmitic and butyric acid molecules calculated from the molecular volumes assuming three different shapes. The hydrocarbon tail is taken as spherical, cylindrical or of the form of a hexagonal prism, this latter shape being useful when considering molecules packed in surface films.

TABLE II

DIMENSIONS OF PALMITIC AND BUTYRIC ACID MOLECULES

	Palmitic Acid $C_{15}H_{31}COOH$	Butyric Acid C_3H_7COOH
Molecular weight	256.	88.
Density	0.85	0.96
Volume per molecule	497. A^3	150. A^3
Sphere		
Diameter	9.83 A	6.59 A
Total surface	304. A^2	136. A^2
Surface of head	45. A^2	45. A^2
Surface of tail	259. A^2	91. A^2
Section of tail	76. A^2	34. A^2
Cylinder with Hemispherical Ends		
Diameter	5.04 A	5.04 A
Length of cylindrical part	21.50	2.80
Total surface	420. A^2	146. A^2
Surface of head	45. A^2	45. A^2
Surface of tail	375. A^2	101. A^2
Transverse section of tail	20. A^2	20. A^2
Longitudinal section of tail	108. A^2	34. A^2
Hexagonal Prism		
Side of hexagon	2.64 A	2.64 A
Total surface	420. A^2	146. A^2
Transverse section	20. A^2	20. A^2
Longitudinal section	108. A^2	34. A^2

The surface energies of these molecules in various environments have been calculated from the data in Table II by means of the assumed values of the γ's and the results are given in Table III. The assumed locations and orientations are illustrated diagrammatically in Fig. 1, in which the numbers correspond to those in the first column in Table III. The relative lengths and diameters shown in Fig. 1 agree with those given for palmitic acid in Table II except that the molecule marked 6b illustrates the butyric acid molecule in a cylindrical form.

As an example of the method of calculating the surface energy let us consider Case 10 in which a molecule of palmitic acid is adsorbed on a water surface. The hemispherical upper end of the molecule which extends above the water has a surface of 40 . A^2 and since the surface energy γ_R is 50 this part of the molecule contributes 20 . $\times 10^{-14}$ erg. The surface of the chain in contact with the water is $375 - 40 = 335$, and the surface of the head is 45. The surface of water destroyed by the presence of the molecule is 20, so that the total energy, obtained by multiplying these surfaces by the corre-

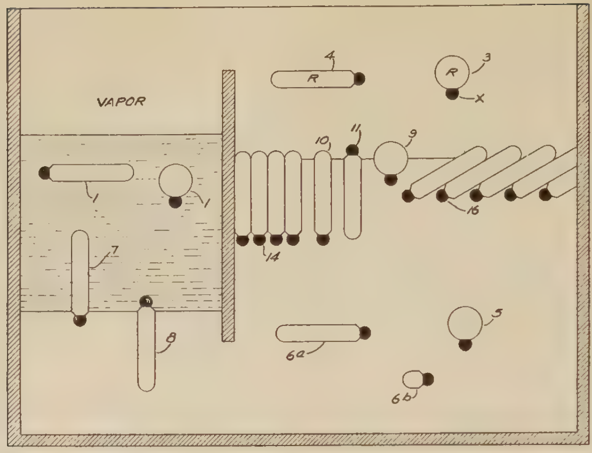

FIG. 1.—Diagram illustrating the various locations and environments of molecules considered in Table III.

TABLE III

SURFACE ENERGIES OF PALMITIC ACID AND BUTYRIC ACID MOLECULES IN VARIOUS ENVIRONMENTS. (See Fig. 1.)

Case No.	Location of Molecule	Shape and Orientation	Surface Energy Palmitic Acid — 10^{-14} Erg	 Butyric Acid — 10^{-14} Erg
1.	In liquid hydrocarbon	Sphere or Cylinder	9	9
2.	In its own liquid (palmitic or butyric)	Cylinder	8	6
3.	In vapor phase (head exposed)	Sphere	189	111
4.	" " " " "	Cylinder	252	115
5.	In water	Sphere	139	40
6.	" "	Cylinder	208	46
7.	At interface between water and hydrocarbon	Cylinder, vertical, *X* down	—37	—37
8.	At interface between water and hydrocarbon	Cylinder, vertical, *X* up	207	45
9.	Adsorbed on water surface (single molecules)	Sphere (half immersed)	39	—4
10.	Adsorbed on water surface (single molecules)	Cylinder, vertical, *X* down	181	19
11.	Adsorbed on water surface (single molecules)	Cylinder, vertical, *X* up	236	74
12.	Adsorbed on water surface (single molecules)	Prism, horizontal	64	1
13.	Adsorbed at edge of film	" "	— 4	— 8
14.	" " " " "	" vertical	—17	—17
15.	" in single vacancy in film	" horizontal	—78	—32

sponding γ and adding is $(40 \times 50) + (335 \times 59) + (45 \times -30) - (20 \times 117) = 181. \times 10^{-14}$ erg.

In Case 2 where we consider a palmitic acid molecule in liquid palmitic acid we assume a random distribution of the molecules of the liquid. Each molecule has a tail having a surface of 375. while the surface of the head is 45, the head thus occupying 10.7 per cent of the whole surface. Considering the tail of a given molecule, we thus conclude that 0.107 of 375 or 40.2 is the area of the tail in contact with the heads of neighboring molecules while the remainder of the tail is in contact with other tails and therefore has no surface energy. Similarly we see that 0.107 of 45 or 4.8 is the area of the head in contact with other heads, while the remaining 40.2 of surface is in contact with tails. Thus the surface energy $2 \times 40.2 \times 20 \times 10^{-16} = 16.1 \times 10^{-14}$ erg is associated with the molecule we are considering. Only half of this energy, however, can properly be attributed to this molecule for if these interfaces are destroyed by removing the molecule (leaving a cavity) half the energy in question (viz. $8. \times 10^{-14}$) can be recovered by allowing the cavity to collapse. Thus $8. \times 10^{-14}$ erg represents the surface energy of a palmitic acid molecule when surrounded by similar molecules.

Case 14 deals with a molecule oriented vertically at the edge of a surface film of similarly oriented molecules. The molecules are assumed to be hexagonal prisms arranged like the cells in honeycomb. On the average each new molecule added to the edge of the film makes contact with the molecules already present on three of the six faces of the prism. Three of the old faces are thus destroyed and three new ones are produced so that the lateral area of the edge of the film (whether in contact with vapor or water) is not altered by the presence of a new molecule. The change in surface energy due to the new molecule is thus:

1. The energy of the upper end in contact with vapor. This area may be estimated as $30 \times A^2$ so that the energy is $30 \times 50 = 15 \times 10^{-14}$.
2. The energy of the head in contact with the water. We may assume that the area $30. A^2$ is in contact with the water while the remaining $15. A^2$ of the head is in contact with the adjacent heads. This energy is thus $30 \times -30 = -9. \times 10^{-14}$.
3. The energy due to the water surface destroyed which is $-20 \times 117 = -23.4 \times 10^{-14}$.

The total energy of a palmitic acid molecule at the edge of a film is thus $15 - 9 - 23.4 = -17.4 \times 10^{-14}$ erg.

In Case 13 the new molecule at the edge of the film is assumed to lie horizontally being in contact with the other molecules of the film only over one of its six faces.

Case 15 deals with the change in energy when a molecule is removed from a surface film of horizontally packed molecules (not at its edge) so as to leave a vacancy.

An examination of the surface energies λ of the molecules in various environments as given in Table III shows that they explain many of the properties of these substances. The small difference between λ in Cases 1 and 2, being less than the value of kT (4×10^{-14} erg at ordinary temperature), indicates that both palmitic and butyric acids should be miscible with hydrocarbons in all proportions.

It is of interest to note that the difference between λ for a molecule in a hydrocarbon and in its own liquid increases as the chain becomes shorter. An example of an effect of this kind, sufficient to lead to relative insolubility, is observed in the case of methyl alcohol which is miscible with hexane in all proportions only at temperatures above 43° C.

The solubility of palmitic acid in water is immeasurably small while butyric acid mixes with water in all proportions at temperatures above $-2.5°$ C. These facts are in general accord with the values of λ given under Case 5. Comparing these with the values for the corresponding hydrocarbons (Table I) we see that the introduction of the carboxyl group lowers the value of λ by 40 units. This accounts for the great increase in solubility.

Comparing Cases 5 and 6 we conclude that the tail of the palmitic acid molecule in water must assume a nearly spherical form while with the butyric acid molecule, thermal agitation will be able to cause the tail to spread out as a chain.

The most interesting applications of the data in Table III are in connection with the arrangements of molecules in surface films. Comparing Cases 2, 5, 7 and 8 we see that the decrease in energy corresponding to Case 7 is so great that practically no molecules could exist in either a water phase or a hydrocarbon phase until the interface becomes saturated with molecules which are all oriented with their heads in the water phase. The relative number of molecules having this orientation as compared to those having the reverse orientation (Case 8) is found from the Boltzmann equation to be as $10^{26}:1$ for palmitic acid and $10^{9}:1$ for butyric acid.

In a similar way we may estimate the probabilities of the various possible orientations of molecules adsorbed at the free surface of water. The high value of λ in Case 11 in which the molecule is oriented vertically with the carboxyl group uppermost shows that no molecules can be in this position.

Without such analysis as we are now making it might seem that single molecules of palmitic acid adsorbed on the surface of water would take up a vertical position as is illustrated in Case 10, the carboxyl group being downwards. In fact N. K. Adam as one result of work described in a series of valuable papers [13] concludes that "expanded films are two-dimensional gases" * in which there is considerable space vacant between the molecules and that in these films "the molecules are oriented perpendicular to the water surface." † An examination of Table III shows, however, that the value of λ corresponding to this orientation has the high value of 181, while for a molecule lying flat in the water surface (with the carboxyl group turned downward into the water at one end of the molecule) λ is only 64 (Case 12). A slightly lower energy ($\lambda = 39$) is calculated (Case 9) for spherical molecules half immersed in the water surface. But the *a priori* probability of the spherical form (particularly in case of butyric acid) is so much less than that of the spread-out form of a molecule which lies flat, that this latter form becomes the more probable.

This conclusion that the hydrocarbon chains of adsorbed molecules lie flat in a water surface was reached by the writer in 1917 [14] from a study of Taube's and Szyszkowski's data on the surface tensions of dilute aqueous solutions of fatty acids and other aliphatic compounds. The energy change involved in the transfer of a $-CH_2$ group from the interior of the solution to the surface was found to be constant and equal to 625 calories per gram molecule or 4.3×10^{-14} erg per molecule.

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* See paper by G. Friedel, this volume, p. 102. Some of the structures he describes may be one or two dimensional solids. J. A.

† In a footnote in his last paper Adam rejects the suggestion that I had made to him that the molecules in expanded films tend to lie flat on the water surface becoming overlapped if sufficiently crowded. He says "There is the more probable alternative, however, that as soon as the molecules have separated, through expansion of the films, they sink in among the water molecules so as to satisfy the attractive forces of the chains. If this is so they will probably remain vertical. Nevertheless it must be remembered that the pressure in two dimensions in the surface is only about one sixth of that expected from the gas laws, and no satisfactory explanation of this fact is at present available." The analysis in the present paper shows that a sinking of the molecules does not satisfy the attractive forces, but that the hydrocarbon chains must be in contact with one another whenever possible, otherwise they must lie flat in the surface.

By Table III the difference between λ for palmitic and for butyric acids, due to the 12 CH_2 groups, is 63 for horizontal molecules on water, while for molecules in solution it is 162 for cylindrical and 99 for spherical molecules. Thus the energy of transfer from the interior to the surface is 8.3×10^{-14} for each CH_2 if the molecule in water is cylindrical and 2.8×10^{-14} if it is spherical. The value 4.3×10^{-14} found from the 1917 work lies between these values and is thus consistent with the results given in Table III.

In discussing the spreading of adsorbed films of the higher fatty acids on water and in comparing these films with those of the lower fatty acids, it was pointed out in the 1917 paper that the films produced by small concentrations of the lower acids behaved like two-dimensional gases obeying the gas law

$$Fa = kT. \tag{6}$$

Here F is the spreading force (dynes per cm.) and a is the area (in cm.^{2}) per adsorbed molecule. It was found that

> "in the case of the higher fatty acids the films do not spread upon the surface in the way required by this equation. Thus with palmitic acid the force F falls to 0.2 dyne per cm. when $a = 23$ A^2 whereas by the equation the force should be 17.5 dynes per cm. for this value of a.
>
> "Any solid or liquid film must have a certain tendency to spread on the surface by giving off separate molecules which follow the gas laws. This tendency may be measured as a 'surface vapor pressure.' With palmitic acid and higher fatty acids this pressure is less than 0.1 dyne per cm. The smallness of this pressure for the higher fatty acids must be due to attractive forces between the molecules powerful enough to prevent their separation. These same forces tend to prevent the film from evaporating from the surface into the vapor phase and from going into solution in the water. There are thus intimate relationships between the lowering of surface tension produced by fatty acids and the vapor pressures and solubilities of these substances. These relationships will be discussed in more detail in another part of this paper."

It was intended to publish the work here referred to as Part III of the paper on the Constitution and Fundamental Properties of Solids and Liquids, but war work which began at that time prevented the carrying out of this plan. The present paper, however, deals with this subject in the manner that was then contemplated.

It was also shown in the 1917 paper that a film of palmitic acid on water at 16° C. resists compression with a force greater than 1 dyne per cm. only when a, the area per molecule, is less than 21 . A^2. But if the water is heated to 45° the film resists compression when a is 33 . A^2 and a similar value of a is found at 16° if a very small amount of acid is added to the water. Thus adding acid or raising the temperature causes the film to expand if the applied compressional force is not over 10 or 20 dynes per cm. Adam has called such films "expanded films." He believes, as we have seen, that the molecules in these films are in the condition of a two-dimensional gas and that the molecules are oriented vertically. Let us see what light is thrown on these questions by the calculations of Table III.

A palmitic acid molecule at the edge of a film of vertically close-packed molecules has an energy $\lambda = -4$ if the molecule is horizontal (Case 13) and $\lambda = -17$ if the molecule is vertical (Case 14) like those in the rest of the film. Thus the vertical orientation is the more probable. An isolated molecule lying flat in the surface (Case 12) gives $\lambda = 64$. The difference 81 is so great that the conclusion may be drawn that practically no molecules will exist isolated in the surface layer but that they will all exist in clusters in which the molecules have their hydrocarbon chains in contact with each other. These values of λ thus explain the observed fact that the two-dimensional gas pressure is negligible for palmitic acid films.

With a lower fatty acid such as butyric acid, however, the difference in energy between an isolated molecule in the surface and one located at the edge of a film is only 18 units so that it is not surprising that with these lower fatty acids the molecules, at least in dilute solutions, do follow the laws of two-dimensional gases.

That isolated molecules of palmitic acid in a water surface cannot exist in appreciable numbers is thus proved by the data of Table III and by the experimental observation that for values of a greater than say $40A^2$, the spreading force is immeasurably small. Thus Adam's view that the expanded films consist of molecules which are largely isolated cannot be correct. What is then the proper explanation of the expanded films?

In the 1917 paper in discussing the arrangement of molecules in adsorbed films on the surfaces of fatty acid solutions it was concluded (page 1888) that in dilute solutions "the hydrocarbon chain lies spread out flat on the surface of the water, but as the concentration of the solution increases, the molecules become more closely packed and when the surface becomes saturated, the molecules are all arranged with their hydrocarbon chains placed vertically." The transition between the two states was assumed to take place in the manner that was suggested (on page 1865) for the expanded film of oleic acid, viz., in the expanded film "the molecules are partly reclining on the surface, while in the second case (compressed film) they are packed tightly side by side and are more or less erect upon the surface."

The area covered by a vertically placed palmitic acid molecule is about $20 . A^2$ while the same molecule lying flat on the surface should cover an area of about $108 . A^2$ (see Table II). Clearly then the expanded film occupying an area of at most $40\ A^2$ must consist of molecules which are only slightly inclined from the vertical. As a matter of fact there is no reason at all why the flexible hydrocarbon chains should orient themselves at any particular angle. They will be quite free to respond to thermal agitation and arrange themselves nearly in the same random manner as in a liquid hydrocarbon, the only restriction upon their motion being imposed by the condition that the *lower end* of each molecule must remain in contact with the underlying water. We can thus readily see why the expanded films are *always liquid* while the contracted or fully compressed films of vertically oriented molecules are frequently *solid*. Taking the volume of the hydrocarbon chain in the palmitic acid molecule as $450A^3$ (Table II) we see that the thickness of the hydrocarbon layer (in A units) will be $450 \div a$ where a is the area of the film per molecule (in A^2 units). Thus when $a = 20A^2$ the thickness is 22.5A while for an expanded film for which $a = 33A^2$ the thickness is 13.6A. Such an expanded film is represented diagrammatically by 16 in Fig. 1, the area per molecule corresponding to the inclination shown being about $a = 60 . A^2$.

Consider an expanded film as covering a definite area of a water surface. If additional palmitic acid molecules are introduced into the film there is no change in the area of the free hydrocarbon surface. The energy of transfer of a molecule from any given location to an expanded film is thus the same as the energy of transfer of the molecule to an interface between hydrocarbon and water as illustrated by Case 7 in Table III and Fig. 1. According to the data of Table III the value of λ for a molecule of palmitic acid at the edge of a condensed film is -17 (Case 14) while for a molecule in an expanded film (Case 7) λ is -37. This would indicate that the expanded film should form in preference to the condensed film. However, the difference of 20 in the values of λ is not greater than the probable error so that the sign of the difference is somewhat uncertain. In considering the stability of expanded films we must take into account the applied compressive force and the effect of the forces acting between the heads of the molecules which are located in the interface between the hydrocarbon film and the water. To understand these relationships better let us analyze the problem as follows.

Let n molecules of a substance (which spreads on water) be present per unit area as an expanded film on the surface of water. The flexible hydrocarbon tails of the molecules are subject to little or no constraint except that due to the fact that they are attached to the heads which are constrained to remain in contact with the water. This constraint may well influence the degree to which the thermal energy of agitation of the hydrocarbon tails aids in spreading the film and may thus alter the relation between the total energy and the free energy which should be used in connection with the Boltzmann equation. But as a first approximation we may ignore such an effect of the thermal agitation, especially as we are willing to regard the surface energies γ_R, etc., as empirical quantities.

The expanded film may thus be looked upon as a layer of hydrocarbon liquid having at its upper surface a surface energy γ_R and having adsorbed in its interface with the water n active groups, or heads per unit area. Consider now that by means of a *two-dimensional piston* (for example a paper strip on the surface) the expanded film is allowed to cover only a part of the surface of the water. The spreading force F (in dynes per cm.) exerted by the film is measured by the mechanical force applied to the piston. On one side of the piston is a surface of water which exerts a force γ_W tending to cause the film to expand and on the other side is the expanded film whose *upper surface* exerts a force γ_R while the *lower surface* exerts a force which we may represent by γ_L. Thus for equilibrium we have

$$\gamma_W - F = \gamma_R + \gamma_L. \tag{7}$$

If the molecules in the film did not have any active groups, the surface tension γ_L would be equal to the normal interfacial energy γ_{RW}. But the *active groups in the interface* because of their thermal agitation will tend to act like a two-dimensional gas. When these active groups or heads are far enough apart they will exert a force F_L following the gas law

$$F_L = nkT. \tag{8}$$

When the molecules are packed as closely as in the ordinary expanded film, we should, by the analogy with the b term in the van der Waals equation, write

$$F_L(a - a_0) = kT \tag{9}$$

where a_0 is the area per molecule for a highly compressed film.

Furthermore, the analogy with the equation of state for gases would suggest that when the film is compressed sufficiently, attractive forces between the active groups would come into play and that these might be largely responsible for the small spreading forces observed with some contracted films. In any case, however, we may place

$$\gamma_L = \gamma_{RW} - F_L \tag{10}$$

and thus from Equation 7 we get

$$F = \gamma_W - \gamma_R - \gamma_{RW} + F_L. \tag{11}$$

For very low compressive forces we may neglect the attractive forces between the heads and thus by combining Equations (11) and (9) we get

$$(F - F_0)(a - a_0) = kT \tag{12}$$

as our equation of state for expanded films. Here F_0 is used as an abbreviation for the three γ terms in (11) so that

$$F_0 = \gamma_W - \gamma_R - \gamma_{RW}. \tag{13}$$

Thus we see that we should not expect the simple gas law of Equation 6 to hold for expanded films, but such a law should hold only after constants F_0 and a_0 have been subtracted from the observed values of F and a.

Examination of the experimental data on expanded films in my 1917 paper, and in Adam's papers, shows that the agreement with Equation (12) is very satisfactory. For large compressive forces deviations occur which are of the kind that are to be expected as a result of attractive forces between the heads of the molecules.* For example, Adam's curve (in this 3rd paper) for a film of myristic acid on water at 32.5° C. gives the equation

$$(F + 13)\ (a - 18) = kT$$

The value of a_0 is thus 18 . A^2 while F_0 has the value -13 dynes per cm.

Let us compare this value of F_0 with that calculated by Equation (13). For water at 32.5° the free energy (surface tension) γ_W is 71.0 dynes per cm. The interfacial free surface energy γ_{RW} of octane is 50.4. Since the temperature coefficient is very low the total interfacial energy is about the same as the free energy. Our theory of the structure of the interface leads to the conclusion that the *total energy* is independent of the length of the hydrocarbon chain and since in this case the free energy and total energies are nearly the same the free energy will also be independent of the chain length. Thus for tetradecane (the hydrocarbon corresponding to myristic acid) we may put $\gamma_{RW} = 50.4$.

The free surface energy of octane at 32.5° is 20.4 and the total energy is 48.4. For tetradecane the theory indicates that the total energy will also be 48.4. The free surface energy is a linear function of temperature and becomes zero at the critical temperature. Taking the critical temperature of tetradecane as 680° K. we can thus estimate that the free surface energy at 32.5° C. should be 26.8.

These values for the γ's give $F_0 = +0.2$ for octane and $F_0 = -6.2$ dynes per cm. for hexadecane. This latter value does not differ greatly from that calculated from Adam's data on the myristic acid films ($F_0 = -13$).

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* A fuller analysis of the experimental data on expanded films will be made in connection with a paper which is being prepared for the 3d Colloid Symposium to be held at the University of Minnesota in June, 1925. See 3rd Colloid Symposium Monograph (Chemical Catalog Co., 1925).

The difference is not greater than should be expected because of the uncertain part played by thermal agitation in the spreading of surfaces.

According to Equation (12) with negative values of F_0, the expanded film should not expand indefinitely even if the compressive force F is made negligibly small. Placing $F = 0$ we see that the maximum area covered per molecule will be

$$a_M = a_0 - \frac{kT}{F_0}. \tag{14}$$

For the case we have considered where $a_0 = 18$ and $F_0 = -13$, we obtain $a_M = 18 + 32.3 = 50.3 \text{Å}^2$ as the maximum area for an "expanded film" of myristic acid on water. This equation shows that the maximum area a_M depends principally upon F_0. By Equation (13) we see that F_0 is the difference between two relatively large quantities which are nearly equal. A very small percentage change in γ_R causes a relatively large change in F_0 and therefore in a_M. As a matter of fact Adam finds that a_M varies only moderately for different substances. As the length of the chain increases he finds a slight decrease in a_M and considers this a strong argument against the view that the molecules tend to lie flat if they have sufficient room to do so. We have seen, however, by our comparison of octane with tetradecane that γ_R and therefore $-F_0$ increase with the length of the chain, and therefore by Equation (14) a_M should actually increase as the chain is made shorter. The changes in a_M observed by Adam may be accounted for by very small percentage changes in γ_R.

Another factor which may need to be taken into account is that the value of γ_R for the CH_3 groups at the ends of hydrocarbon chains (particularly noticeable in iso-compounds) is about 10 per cent lower than for the CH_2 groups constituting the central portions of the chains. Thus as a film becomes more expanded the value of γ_R increases, tending to make the equilibrium of such a film more stable. Of course an expanded film can be dealt with by equations of the type we are now considering only as long as the upper surface forms a continuous hydrocarbon surface. The area of such a film is thus limited to that given by the molecules when they lie flat in the surface.

This theory of "expanded films" requires that the molecules remain in contact while Adam concluded that in such films the "molecules become separated and move about independently on the surface" and that "there are spaces not covered by molecules." Adam considered that the molecules of the film behaved as a two-dimensional gas while we conclude that it is only the heads of the molecules that behave in this way.

It is hoped that the illustrations given in this paper have helped to prove the usefulness of the conception of separate surface energies for each of the different parts of complex molecules. It is believed that this viewpoint is applicable to the study of nearly all the physical properties of organic compounds, particularly to the calculation of the vapor pressures, solubilities, viscosities, and surface tensions of liquids and their mixtures.

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Physics, Chemistry and the Colloidal State

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From the very outset of investigations on the colloidal state, there has been a tendency to regard reactions occurring between colloids and foreign substances as being governed by chemical laws, even admitting that the colloidal state is characterized by distinctly individual and novel properties. Hence arose the expression "Colloid Chemistry." It is still used by certain authors now when physics is encroaching upon chemistry, in order to make it possible to fathom the nature of chemical reactions and to apply exact methods at a time when a particularly interesting and important new science—Physical Chemistry—was making more and more striking advances.

Thus there were undertaken innumerable investigations whose object was to determine the physical constants and the chemical composition of colloids. Today all these investigations are obsolete, because they reached no concordant result.

By way of illustration we might recall the numerous attempts to determine the molecular weight of colloids. Considering the resulting figures, so discordant that they varied, according to author or preparation, as one to a hundred (glycogen from 1,600 to 200,000), it is evident that the chemical methods used in determining molecular weights are useless when applied to colloids.†

We might add that practically the same is true with regard to the osmotic pressure of colloids.

Nevertheless, we see from time to time attempts to subordinate colloidal reactions and the properties of colloids, solely to the laws of classical chemistry. Grimaux, Wyrouboff, Nicolardot, Reychler, Wo. Pauli, Jordis, J. Duclaux and others have striven to prove that the colloidal micell is ionized, and that all reactions, occurring between the micell and reagents, are only classical chemical reactions.

The ideas of these authors have not been favorably received by scientists specializing in this field, nor have they been closely examined. This is a mistake; for among their conclusions are some that should be known. Furthermore, rigid analysis always permits us to fortify ourselves against the fallacious premises of certain methods supposed to be rigorous, and to take a just measure of many apparently convincing theories. Quite recently two scientists, Sörensen and Loeb, have advanced in favor of the chemical theory of colloids, views that should be closely examined. In order that we may have a clear idea of their experiments, let us consider, first, the ideas above referred to.

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* Translated by Jerome Alexander.

† Among the causes of these disparities were neglect of such factors as degree of purity, freedom from electrolytes, H ion concentration, etc. J. A.

Views of E. Jordis.

A general and very complete outline of this question was given by Jordis in 1904. He started from the following assumptions: (1) aqueous solutions are very complicated mixtures of numerous substances; (2) the occurrence of a reaction is not dependent upon the absolute quantity of an ion, but upon its presence; (3) every chemical equation contains numerous hypotheses, mainly that all constituents concerned in the reaction are connected by conditions of equilibrium.

With the case of a solution of $CuSO_4$ in water, we have:

$$CuSO_4 \rightleftarrows Cu^{++} + SO_4^{--}.$$

Water may give rise to two reactions:

$$(1) \quad Cu^{++} + H^+OH^- = OH^-Cu^{++},\ H^+$$

$$(2) \quad \begin{cases} SO_4^{--} + H^+OH^- \rightleftarrows HSO_4^-,\ OH^- \\ SO_4^{--} + H^+OH^- \rightleftarrows SO_4^{--} + H^+ \rightleftarrows HSO_4^- \end{cases}$$

and in accordance with dissociation, other combinations may occur.

The second assumption made by Jordis and later taken up by Duclaux, is the necessity of the presence of foreign ions for the stabilization of colloids.

Considering the variety of chemical reactions which occur even with solutions of electrolytes, it is no wonder that with substances infinitely more complicated, as are colloids, their mechanism and nature should quite escape us. Being a cautious experimenter, Jordis emphasized the fact that in colloidal reactions, and particularly in flocculation, other phenomena played a rôle: the electric charge of ions, their valence and surface phenomena; that is why only nondissociated substances are inactive.

Finally, he himself pointed out the difficulty of explaining everything by chemical reactions, and the phenomenon of periodic flocculation remained an enigma to him.

In short, in promulgating his hypothesis Jordis well appreciated that it did not agree with all the facts then known, and he agreed rather with the statement of Graham:

"There are no abrupt changes in nature, and the division between different classes is never absolute."

Of a much more chemical nature are the views of the successors of Jordis: Wyrouboff, Nicolardet, Reychler, J. Duclaux and others.

Views of J. Duclaux.

Among these, J. Duclaux is most trenchant and typical. Knowing that electrolytes differ among themselves, imagine the diversity with colloids. After opposing in very strong terms those authors (Zsigmondy, Perrin, Smoluchowski, Einstein), who regard the size of micells as the essential characteristic of the colloidal state, and who consider surface tension and electric charge due to contact, J. Duclaux, without giving irrefutable proof, advances the opinion that colloids composed of micells of uniform size, such as colloidal gold, albumin or ferric hydroxide, have not the same physical and chemical properties; whence he deduces that in these cases the constitution of the micells ought to be different.

This opinion is quite inaccurate. We know the difficulties encountered by physicists in trying to obtain hydrosols with micells of uniform size; even the meticulous experiments of Perrin on the hydrosol of gum gamboge did not in this respect satisfy Smoluchowski.

In studying the structure of the colloid micell, the supporters of the chemical view quite naturally address themselves not to natural organic colloids whose composition is absolutely unknown and whose study is therefore very difficult, but to synthetic colloids. On studying the formation of colloidal arsenic sulphide, and especially of copper ferrocyanide and ferric hydroxide, they concluded on the basis of analytical results, that the reactions are not what had been heretofore supposed.

Thus, to effect total precipitation, we do not need 2 molecules $CuSO_4$ for 1 molecule of $K_4Fe(CN)_6$, but only 1.7; the precipitate formed actually contains 1 molecule of $Cu_2Fe(CN)_6 + 0.18\ K_4Fe(CN)_6$; furthermore the iron in this mixture does not exhibit its usual chemical reactions. In the case of arsenic sulphide, the precipitate contains sulphur.

From the experiments of Linder and Picton (As_2S_3) and of J. Duclaux, it was concluded that the mixtures thus formed could not be mixed salts, since the constituents are masked, and that it was not a case of mechanical entrainment because in the case of As_2S_3 neither the sulphur nor the hydrogen necessary to satisfy the two valences of the sulphur attached to the precipitate, betrayed themselves in the resulting colloid by the odor of hydrogen sulphide!

Apart from this last reason, which we consider very unconvincing, we must recall that where metallic salts are precipitated by H_2S, oxidation always causes the formation of sulphur, as every analyst knows. This sulphur is evidently not ionized, wherefore its two free valences are not saturated by hydrogen. Hence, to put it most strongly, we see in the case of the formation of colloidal As_2S_3 a *fixation* (let us temporarily use this term) of sulphur.

With reference to the presence of foreign substances in the other colloids studied, we must emphasize that the ferric chloride fixed by the micells of ferric hydroxide, can be almost entirely removed by dialysis. Furthermore, the amount of a substance fixed by a colloidal micell varies from one case to another, depending on the conditions of the experiment. We by no means consider that there is justification for the conclusion of the defenders of the chemical view—as we have seen, nothing warrants their statement that the nascent colloid combines chemically with substances in the surrounding medium. The only fact proven is that the particles of a colloid often contain foreign substances or impurities; but there is no theoretical difference from the case where a metal is dispersed by purely mechanical means, without the intervention of secondary substances. J. Duclaux seems to ignore the fact that quite a few colloids have been prepared in this manner, and the work of Plauson indicates that all solids may be dispersed mechanically. Therefore, unless we assume a formation of metallic oxides at the expense of atmospheric oxygen, which would be a very far-fetched scientific argument, the presence of a foreign substance in a colloid is not theoretically necessary.*

These arguments, however, were also used by Jordis. "The water used by Bredig was kept in a crystallizing dish open to the air; it therefore contained impurities. As we know the pure metals had to be cast, and were therefore in contact with gas, and they absorbed gas as earlier investigations have shown. Besides, they contain carbon. The electrodes are handled to bring them into contact, and take up traces of animal and organic matter conducive to the formation of sols. Now when the current is switched on, it not only pulverizes the cathode, but it also electrolyzes the water, conducts alkalis to the cathode, oxidizes organic matter, etc. . . . Furthermore, in the water are oxygen and nitrogen which, even with weak currents, give nitrogen-containing acids. . . ." The proof that such substances exist, Jordis found in the growth of fungi on electrosols, which was noted by Bredig, and in their stabilization by traces of alkali! Without, however, denying the fact of their presence, this is no argument to *prove* that these impurities, homeopathic at most, are of any use or indeed a *necessity*.

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* They increase the stability of the colloid, and add to its *life*. See also papers by von Weimarn, Utzino, and Hagiwara, in this volume. J. A.

The proponents of the chemical hypothesis, disregarding this basic fact, then ask what rôle we must attribute to the impurity always present in colloids.

"There are two ways of handling this impurity. We may neglect it, assuming that it plays no rôle. Or else we may assume that this same impurity in reality plays an essential rôle; it is the sole active part of the colloid, the balance being merely a mass of inert molecules." (p. 88.) *Tertia non datur.* And here are the accumulated proofs.

In the first place consider the phenomenon of coagulation (gelification) of colloids, especially the examples studied by Graham (silica) and Malfitano and Duclaux (ferric hydroxide). We see that on dialyzing these colloids the fixed impurity is eliminated, but at the same time the micells increase in size, the colloid becomes more susceptible to coagulation by electrolytes, and the changes suffered by the influence of physical agents (temperature) become irreversible.

We might observe that the facts stated are not general. Dialysis does not always make colloids labile; thus the colloids made electrically are quite resistant to dialysis, and better still, the presence of electrolytes makes them labile. Further, if the presence of electrolytes is sometimes necessary for the stability, or even for the existence of a colloid, there is never the necessity of having *one certain electrolyte;* and, along this line of thought, no one denies the importance of the electric sign of the stabilizing electrolytes. Finally, the recent work of Sörensen, Loeb and others, has shown that, at their isoelectric point (singular or plural), certain colloids have their physical properties most suppressed, and that their stability is then very slight. From the facts stated only the following conclusion can be drawn: *Sometimes, certain colloids demand the presence of an electrolyte to insure their stability.*

Upon the basis of the researches of Linder and Picton, of Nicolardot and of Bechamp, J. Duclaux claims that on coagulation, the impurity fixed by the colloid leaves it, and is replaced by the coagulating substance "in equivalent quantity." He extended these experiments, studying the coagulation of ferric hydroxide; and generalizing from these three cases, drew the conclusion that coagulation is a chemical reaction between the impurity fixed by the colloid and the coagulating substance.

Here J. Duclaux forces the facts extremely. In the first place, does his method admit of strict conclusions? By no means. What is this method? A colloid is analyzed quantitatively and ultrafiltered; and the ultrafiltrate is analyzed. Now this ultrafiltrate is far from representing the intermicellular fluid, for the phenomenon of adsorption by the membrane is without doubt a factor in ultrafiltration, as has been shown by Malfitano and Lottermoser, notwithstanding statement of Bachmann to the contrary.* Then the colloid is coagulated, and the preceding analyses are duplicated. The value of these analyses is doubtful. In the first place, if the author had ultrafiltered even

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* See also H. Bechhold in this volume. J. A.

1 liter of gelatinized ferric hydroxide, he would be using a quantity containing only centigrams of the substances sought (1 mol $Fe_2Cl_6 + 70$ mol Fe_2O_3, that is about 5 per cent); furthermore, ultrafiltration of a gel is quantitatively a very uncertain operation.

And even assuming that the results obtained are correct, we would be confronted by a most curious chemical reaction. Indeed, according to Duclaux himself, a colloid may be coagulated by any electrolyte or even by non-electrolytes, and in the coagulated colloid the first coagulant may be replaced by others. Thus, according to Linder and Picton, if As_2S_3 is flocculated by a barium salt, this can be replaced in the flocculate by a calcium salt; better yet (to eliminate the question of valence in these replacements), if a sol of this colloid is precipitated by Co ions, these may be replaced by Ca; if by a Ca ions, these may be substituted by cobalt ions.

J. Duclaux coagulated a copper ferrocyanide hydrosol by one molecule of $CuSO_4$, and the precipitate contained 100 atoms of Cu. Perrin points out that on coagulating As_2S_3 hydrosol with lanthanum, the coagulum contained 1 atom of lanthanum to 425 atoms of As (p. 69). He therefore asks: "shall we admit for instance that we have a definite compound, containing over 400 atoms of arsenic to each atom of lanthanum? . . . Furthermore, if this useless and complicated hypothesis were not withdrawn, its rejection would be forced if it were shown that the composition of a coagulation can vary in a continuous manner." (p. 71.) This has been definitely proven.

The supporters of the chemical theory have themselves found many difficulties in their line of argument. "In any event," said Duclaux, "it is remarkable that the molecules of As_2S_3 do not take part in anything" (p. 98); then, contradicting himself (p. 33), he considers that coagulations of colloids "are evidently far removed from crystalloids, and resemble but slightly chemical reactions observed in true solutions: for there we would have only those specific precipitations on which analytical chemistry is founded."

We are entirely of this opinion, and that is why we cannot follow J. Duclaux when he regards coagulation as a chemical reaction, and we do not believe that the formulæ he proposes ($n As_2S_3$, $x H$) in order to illustrate the reaction in colloidal coagulation, can be accepted by a single chemist.

However, it must be added that other arguments are advanced in favor of considering the colloid micell as an ionized body: these are experiments on the electric charge of colloids, their conductivity, and their osmotic pressure. The answer to these is quite simple. Thus the charge of colloids may originate from other causes than ionization of the micell; and the fact that suspensions carry a charge and that water is displaced by a current when it traverses capillary tubes are demonstrations of it. The phenomenon of electrification by contact, which no one denies, is lost sight of by J. Duclaux.

The auto-conductivity of micells is very uncertain. It is of the order of 10^{-6}, and is estimated as the difference between the conductivity of the colloid and that of the liquid obtained by ultrafiltration, just as though the collodion membrane took no part in this ultrafiltration. Besides considerable variations occur in the conductivity of water upon storage in flasks, and this factor involves appreciable causes of error as has recently been shown by Lasseur and Girardet. The author regards this procedure as "a rigid method," but himself is of the opinion "that it is not absolutely rigorous." (p. 109.)

As to the method employed by J. Duclaux to determine the osmotic pressure of colloids, the neglect of hydrostatic pressure, the employment of the ultrafiltrate as external liquid, and the omission from consideration of other sources of error such as inequality in the permeability of two colloidion sacs, and notwithstanding maintenance of experimental conditions, the slight pressures observed (centimeters); the variation of this pressure with different samples of the colloid (p. 208)—all these subvert the rigorousness of the determinations.

Views of Sörensen.

Certain authors sometimes invoke the researches of Sörensen to support the chemical view of the colloidal state. Let us see if this is permissible.

S. P. L. Sörensen set out to conduct researches on organic colloids with extreme precision, and in this he has fully succeeded. This precision, absolutely necessary to rigorous conclusions, was directed first to the purity of products, and then to the experimental method. No exception can be taken: the product was pure, crystallized; the experimental method (measuring ionic concentration, and above all measuring osmotic pressure) irreproachable. Consider the conclusions of this author. You will find no bias, no exaggeration, but the simple and logical statement of facts. What are these facts?

Firstly, the product obtained by Sörensen—egg albumin crystallized in presence of ammonium sulphate—"always contains a fairly large amount of ammonium sulphate" (p. 597); "dialysis cannot remove all this salt and there always remains about 1 per cent" (p. 599); "what is worse, the two components of this salt, ammonia and sulphuric acid, do not remain in equivalent quantities" (p. 600); "it is possible to eliminate only one of them" (p. 600).

Regarding the physical properties of this colloid, the main fact pointed out by Sörensen is the importance of the concentration of H^+ ions, and particularly of the isoelectric point; further, the constancy of its properties, a quantitative constancy found in products of different origin, of different ages, etc., but under the express condition that you work under definite conditions of ionic concentration and content of sulphate of ammonia. Thus the osmotic pressure is always the same (46.8 cm. of water) with all the products, providing there is always 15.6 per cent of ammonium sulphate per gram equivalent of nitrogen per liter, and in addition the H ion concentration is 13.0×10^{-6}.

Some authors are inclined to see here proof of the rigorous constancy of composition on the part of colloids, instead of a disconcerting παητα ρει. But on mature consideration it is easy to discover in an argument like this the following deductive error in the facts pointed out by Sörensen: *the rigorous constancy of the properties of a colloid is not involved, but the constancy of these properties under certain conditions.* The syllogistic error is a flagrant one.

And no one would claim that there is an analogy between the physical properties of any salt, such as its solubility (which is always constant even in the presence of small amounts of foreign substances), and the solubility of the colloid studied by Sörensen, in which a 7 per cent variation of ammonium sulphate reduces the solubility 15 per cent. The constancy of composition and chemical individuality of a colloid will be proven when colloids of different origin, age, etc., are shown to have the same solubility, the same osmotic pressure, the same H ion concentration, etc., just as is the case with organic substances—alkaloids or glucosides obtained from various plants, to take the most complicated cases.

Apart from this general conclusion, Sörensen's researches do not solve the question as to whether colloids have an osmotic pressure or not. Indeed with a hydrosol of crystallized albumin containing about 1 per cent of ammonium sulphate, it is not known if the observed osmotic pressure is nothing but that of the electrolyte.

To conclude, Sörensen's researches once more prove that *it is sometimes impossible to free certain colloids from foreign ions, but these ions are fixed by the colloidal micell in non-equivalent quantities,* and what is still worse, that we can get rid of one of these ions, which may be arbitrarily chosen.

Sörensen himself drew the following conclusion: "I willingly admit that (for the solutions studied) it is possible that there are involved phenomena of a purely physical kind, whose explanation must be sought in the colloidal nature of the solution studied" (p. 594).

Views of J. Loeb.

Let us now examine the work of J. Loeb, which seems to carry new arguments in favor of the chemical view.*

J. Loeb's researches deal with the colloidal properties of proteins, especially of crystallized albumin, casein, and gelatin. This shows that the path followed by the American biologist is the reverse of that followed by Linder and Picton, Jordis, Malfitano, etc., and at once a primary objection comes to mind: is it possible to draw satisfactory conclusions on the basis of researches with indefinite substances, varying from one sample to another? It is hardly likely, as is obviously shown by the obscure points it is impossible to clarify, *e.g.,* the variations in the osmotic pressure of gelatin under the same H ion concentration and experimental conditions (p. 235). The importance of the purity of a colloid, which had not escaped Sörensen and others, was put aside by J. Loeb.

But let us follow his conclusions step by step. At the very beginning he wished to prove that powdered gelatin, crystallized albumin, and casein in aqueous dispersion, fixed neither anions nor cations at the isoelectric point ($pH = 4.7$); and on the other hand that above this concentration only cations could be fixed, and below it only anions. This fixation follows the law of valence.

This statement is nothing new; from the work of Hardy, Hofmeister, Pauli, Michaelis, Dhéré, Rona, and many others, we know that at the neutral point gelatin and proteins are amphoteric, are slightly reactive, and are most unstable. Sörensen and Michaelis have introduced, in place of the idea of neutrality, the apparently more strict expression of "isoelectric point." Applying these ideas to the systemic study of the three substances mentioned, Loeb tries to revise many facts which are considered accurate (Hofmeister series, etc.).† But from these experiments Loeb particularly draws the conclusion that the fixation of foreign substances follows the law of valence and also all stoichiometric laws.

Several limitations to this generalization were brought out by J. Loeb himself, in the course of his argument.

To begin with, certain acids have a peculiar action, acetic acid, for example (p. 59); the action of bases shows no preliminary difference between mono- and polyvalent ions, but this difference appears beginning with a $pH = 8.5$ to 9.0 (pp. 60 to 61). Here then is a first restriction; *the rôle of*

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* See *Revue generale des Sciences,* 33, 610 (1923), for a review of J. Loeb's theory by W. Kopaczewski.

† See paper by L. Michaelis, this volume, p. 471. J. A.

valence is not general, and we are confronted with a specificity of a different kind.

It is furthermore surprising to see J. Loeb try to subordinate the facts above mentioned to the law of equimolecular proportions. He himself cites three very divergent determinations of the molecular weight of gelatin * (768—Procter and Wilson; 839—Wintgen and Krueger, and 11,800—Dakin), and chooses that which best agrees with his views! As an additional safeguard he includes filtration experiments, which are far from being quantitative either methodically or in result, and concludes that "the quantities of acids and bases that combine with proteins, are identical with those which combine with crystalloids. Or in other words, the forces . . . are purely chemical . . . valence." (p. 63)

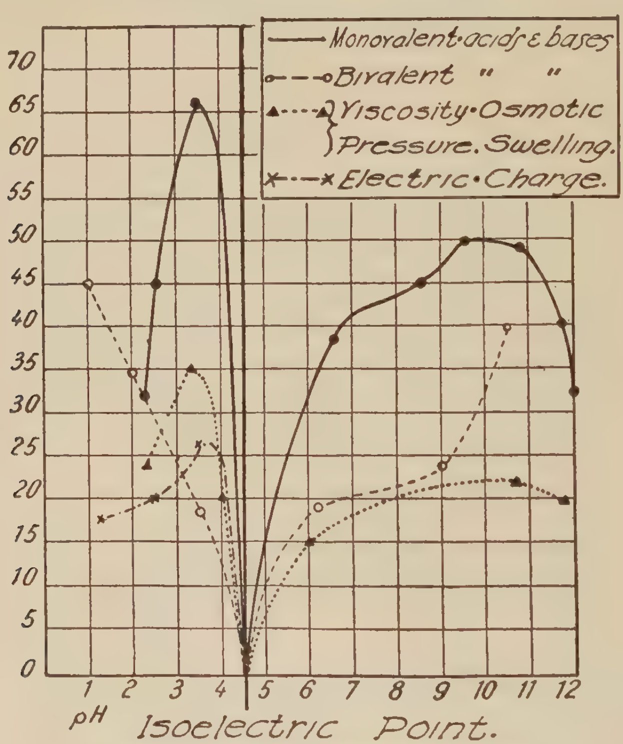

Fig. 1.—Curves showing the properties of gelatin on both sides of the isoelectric point (after J. Loeb).

Referring to the restrictions and the exceptions we have pointed out, we think that this conclusion is not warranted, and that, apart from technical objections to which we will later refer, the only justified conclusion is the following:

The amounts of acids and bases fixed by the proteins studied, depends on the H ion concentration, and seems to be influenced by the valence of their ions.

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* On this question see J. Alexander, Am. Chem. Soc. Monograph No. 11, on "Glue and Gelatin," 1923.

To resume: at the isoelectric point not only is the reactivity of the colloids in question least pronounced, but so are all their physical properties, such as viscosity, osmotic pressure, swelling, electric charge, labilization of their neutral salts, and their stability.

This statement is open to two types of objections. Firstly, objections to the technic. It must be emphasized that the materials used by J. Loeb were not pure and completely free from electrolytes. This has been done, however; for example, Ch. Dhéré has purified gelatin to such an extent that its electrical conductivity is a nominal. Further C. R. Smith and Miss Field have recently described a simple method for completely eliminating electrolytes from proteins.

This presence of electrolytes was not, however, of material importance in the foregoing experiments. It is quite different in measurement of osmotic pressure, electric charge and flocculation, where the presence of these substances may markedly alter the experimental results.

The following objection concerns the experimental technic: except in rare instances, J. Loeb bases his arguments on experiments with concentrations in the neighborhood of the isoelectric point. Now, his own curves, from their shapes, strongly suggest a continuation of these researches, and seem to predict that certain conclusions of the author are at least premature.[*]

Finally, the experimental method of J. Loeb is at times quite rudimentary: along with an exact physical method, the determination of H ion concentration, the author measures viscosity with the capillary tube of Poiseuille-Ostwald, a method shown to be inaccurate by the researches of Scarpa, Hess, Rothlin, etc.; besides which he sometimes determines the viscosity of semi-gelatinous substances (pp. 206-7). In determinations of osmotic pressure he takes no account of hydrostatic pressure, variations in permeability of collodion membranes, etc., errors which we have emphasized in considering the researches of J. Duclaux. The degree of swelling is determined by simply observing the volume (p. 78), instead of using apparatus like that of Posnjak. And sometimes the experimental inaccuracy is disquieting: *e.g.,* measuring the extent of solubility of gelatin by determining differences of two volumes or two weights, before and after filtration.

We must add that experiments on powdered gelatin suspended in water, involve an unbalanced external phase, for it seems to us that solid powdered gelatin, even at 15° C. is not solid, but already is swollen in a more or less pronounced manner. This did not escape J. Loeb, when he warns against exceeding a temperature of 20° C. for "then the gelatin dissolves rather quickly" (p. 153). Better yet, a striking confirmation of this objection appears from J. Loeb's own experiment, especially the curves showing the viscocity of gelatin in function of time (p. 214, Figs. 57 and 58).

If, despite these objections involving principles, the results obtained by J. Loeb seem to be concordant, that is no matter. Every one of his curves has a different point of inflection, after having attained an optimum of all the physical properties referred to above. By combining several curves, we have in 1922 suggested the idea that J. Loeb's statement that colloidal properties are at a minimum at the isoelectric point, is perhaps premature. Figure 1 gives these curves for gelatin.

There is no reason for not supposing that *by extending these researches*

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[*] This was done by W. A. Hoffman and R. A. Gortner; and beyond the limits $p_H = 2.5$ and $p_H = 10.5$ the results were quite different from those found by Loeb. See Second Colloid Symposium Monograph, 1925. J. A.

with additions bringing us still further away from the isoelectric point, we may reach other points of ionic concentration where the properties of colloids are also a minimum. In fact no one should overlook the production of periodic flocculations and coagulations of colloids by increasing amounts of flocculating or coagulating reagents. This phenomenon * has been thoroughly studied by Freundlich, Bechhold, Neisser, etc., on inorganic colloids, by Eisenberg and Volte on the agglutination of typhoid bacilli, and by Vernes and Douris on the flocculation by sera of various inorganic colloids or fine organic suspensions.

Therefore the only conclusion permissible from the experiments of J. Loeb is the following: *The physical properties of colloids, such as osmotic pressure, viscosity, swelling, electric charge, and power to fix various substances, as well as their stability, depend on the H ion concentration. The future will show whether, apart from the isoelectric point, there are not other points where the properties also pass through a minimum.*

J. Loeb studied the rôle of neutral salts on the physical properties of the organic colloids mentioned, and reached the same conclusion as on the subject of acids and bases, that is, that the physical properties of colloids are influenced by the valence of the reacting ions. There are numerous irregularities here, more so than with acids and bases. Thus all the experiments with gelatin show but a distant relation to the two other colloids (p. 71); swelling experiments show exceptional behavior with acetic acid and monovalent bases (p. 80); the swelling of gelatin is less marked in alkalis (?) than in acids, which is not the case with osmotic pressure (p. 81). The electric charge is also sometimes independent of valence; thus the drop in potential of gelatin which has fixed oxalate, equals that between normal gelatin and gelatin which has fixed sodium chloride; in particular, the curves showing differences in potential are different, according to the salts used. While those of phosphates and sulphates, after a second descent outside of the isoelectric point, make a new ascent, the curves of oxalates and chlorides, after reaching an optimum at about pH = 2.2, show an abrupt descent without any new rise (p. 122).

The introduction of equimolecular quantities of salts proves the secondary rôle of the valence of corresponding ions (Fig. 33).

These and other irregularities are explained by J. Loeb as "secondary physical modifications of the gelatin" or as "difference in cohesion of ions in gels," suppositions which, of course, explain nothing.

To sum up, the results published by Loeb do not at all agree with the stoichiometric laws of general chemistry; they agree much more with the hypothesis of adsorption compounds.

We now reach the culminating point of J. Loeb's work. Believing that electrolytes exert the same kind of influence on all colloidal properties, it was but natural to seek the cause of this analogy of behavior. This he thought he found in Donnan's equilibrium.

What is Donnan's equilibrium? When a solution of two salts is separated by a membrane impermeable to one ion of the electrolytes, the diffusible ions distribute themselves unequally on the two sides of the membrane. This unequal distribution should produce a drop in potential and a difference of osmotic pressure.

Suppose, for example, that a membrane separates a solution of NaCl from a solution of a sodium salt whose anion R is not diffusible (it need not be colloidal):

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* See paper by A. Lottermoser, this volume, p. 670. J. A.

$$\begin{array}{c|c} \multicolumn{2}{c}{M} \\ Na^+ & Na^+ \\ \underline{\underline{R^-}} & Cl^- \end{array}$$

In this case, *Na Cl* will diffuse through the membrane *M* and distribute itself as follows:

$$\begin{array}{c|c} \multicolumn{2}{c}{M} \\ Na^+ & Na^+ \\ \underline{\underline{R^-}} & \\ Cl^- & Cl^- \end{array}$$

And this distribution should occur according to the formula deduced from the laws of thermodynamics:

$$(Na^+)^2(Cl^-)^2 = (Na^+)^1(Cl^-)^2$$

Equilibrium can occur, then, only when:

$$(Na^+)^1 > (Na^+)^2 \text{ and } (Cl^-)^1 < (Cl^-)^2$$

According to Nernst's formula,* this unequal distribution of ions should give rise to a potential difference:

$$\pi 1 - \pi 2 = 0.058 \log \frac{(Na^+)^2}{(Na^+)^1} \text{ or } 0.058 \log \frac{(Cl^-)^1}{(Cl^-)^2}$$

This roughly outlines Donnan's theory; it includes also what happens where several nondiffusible ions are present. It is a recent theory: Donnan stated it generally in 1911; in 1914 he pointed out that phenomena did not always follow the theory; in 1919 in applying the theory to work with membranes other than copper ferrocyanide, especially to amyl alcohol, he was not very positive on the strict agreement of calculated results with those found.

Can the concept of Donnan be applied to the study of colloids? Where is the membrane of suspensoid colloids? Can it be applied to the study of emulsoid colloids or of gels? Loeb, considering only these latter, reasons as follows:

The colloidal micell is ionized; it is a complex of ions and molecules which is not necessarily ionized; when a colloid, like gelatin, is separated from its intermicellular liquid by a collodion membrane, a potential difference appears between the two sides of the membrane. Gelatin not being diffusible through the membranes, a Donnan equilibrium should exist. Experiment actually shows that it is possible to explain by the laws of this equilibrium, the appearance of the electric charge as well as the influence of neutral salts and H ion concentration on this potential difference; it is therefore probable that this equilibrium ought to explain not only osmotic pressure, but also all the physical properties of colloids, granting the similitude of the actions of different factors on these properties. Donnan's equilibrium thus becomes *Deus ex machina* for the fundamental properties of colloids (p. 285).

J. Loeb's logical sequence is not correct. In the first place, as we have seen, nothing justifies admitting the chemical nature of the micell. The laws of the Donnan equilibrium may explain the potential difference produced by the presence of a membrane between a colloid and a diffusible liquid: but will they apply when the membrane is absent?

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* Regarding the failure of the Nernst formula, see L. Michaelis, this volume, p. 471, where the Donnan equilibrium is also discussed. J. A.

J. Loeb tries to prove this is so. The results with gelatin are subject to limitations (Tables XVI and XVII, pp. 136 and 134), so that the author himself is forced to say that there is not a quantitative agreement between the observed and the calculated results. But strictly speaking, it might be admitted that the Donnan equilibrium dominates the distribution of ions with a solution of gelatin separated from a diffusible liquid by a collodion membrane. J. Loeb, however, makes a *salto mortale* in applying the concept of this equilibrium to the suspension of gelatin in water, which he considers as a true suspension, dropping the swelling from consideration, small though it be (it cannot be neglected even at a low temperature), and eliminating the membrane.

He reasons as follows: the essential thing in the Donnan equilibrium is *the non-diffusibility of an ion, no matter what the cause of this may be.* When a membrane separates two liquids, the equilibrium is governed by its non-permeability; in the absence of a membrane, cohesive forces may retain an ion and prevent it from diffusing (p. 152).

The logical error in J. Loeb's ratiocination consists in thinking that *"to be prevented from diffusing"* and *"to be unable to diffuse even if free"* mean the same thing. The difference is not an unimportant one. Many forces may weaken cohesion, free an ion prevented from diffusing, effect its diffusion, and abolish Donnan's equilibrium.

The experimental error of J. Loeb makes itself evident by considering a suspension of powdered gelatin in water at 15° C. as a suspension of solid particles like kaolin, animal charcoal, or a metal electrosol. We have emphasized that it must not be forgotten that gelatin swells in the cold. Then, strictly speaking, the external layers of the swollen particles of gelatin may be compared to a membrane separating them from the external liquid. Loeb admits this (p. 279). Here perhaps is the origin of certain analogies between the observed potential differences here and those calculated on the basis of the Donnan equilibrium. These analogies are not quite strict, and J. Loeb does not explain them satisfactorily (p. 254, Tables 24, 25 and 30). But all this has nothing to do with suspensions, nor with colloids whose dispersed phase is insoluble. In such a case the Donnan equilibrium is obviously not applicable; it cannot explain the electric charge on these colloids, just as it cannot explain the phenomenon of the transport of water, or migration in tubes under the action of an electric current. This is why the Donnan equilibrium cannot explain the numerous facts stated by Loeb, such as the appearance of a positive electric charge under the influence of trivalent anions and a negative charge under the influence of tetravalent anions (pp. 164-5), and he is forced to have recourse to an entirely new hypothesis of a "labile combination between gelatin and these ions."

To sum up, admitting that the Donnan equilibrium is definitely established in all its details, admitting the explanation, by its means, of the appearance of a potential difference between a colloid and a diffusible liquid separated by a membrane, admitting even for the sake of exactness, the application of the laws of this equilibrium to swelling colloidal particles, and seeing in it one of the reasons for the electric charge on these particles, it is, *a priori,* illogical to include suspensions and colloids whose dispersed phases are insoluble, and no experimental support for this view is advanced.*

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* Recent researches of the author on electrocapillary phenomena of gels show that swelling is accompanied by changes in the electric potential, analogous to those seen in the vaporization of a true liquid. (*Compt. rend. Acad. des Sci.,* July, 1925.)

From these experiments only one single conclusion can be drawn: *The Donnan equilibrium seems to take part in the appearance of a potential difference between two liquids separated by a membrane which forms an impermeable barrier to one of them; it seems also to play a part in the presence of a charge on solid swollen particles.*

Having thus reached the culminating point, J. Loeb rests on his oars and applying the idea of the Donnan equilibrium to osmosis, viscosity, swelling, and to the action of neutral salts on the stability of colloids, he draws the conclusion that the Donnan equilibrium dominates all these properties.

To put it tersely, all that has already been said of the methods he employed, especially on osmotic pressure, viscosity, flocculation, etc., may be applied with full force to his experiments. And in spite of all this, the results obtained are absolutely insufficient.

According to Loeb himself, swelling is not controlled by the forces of the Donnan equilibrium, nor by the forces of osmosis as Proctor and Wilson would have it; it is determined by "forces which must be different from these."

The influence of H^+ ions, of ionic valence, of salt concentration, and of the viscosity of the colloids studied is *"in reality, the influence of electrolytes on the swelling of solid submicroscopic particles, the proteins contained in the solution"* (p. 231). Granting that this swelling, according to Loeb himself, has nothing to do with the Donnan equilibrium, here then is viscosity apart from this cause.

The flocculation of the proteins studied (coagulation as Loeb calls it) betrays no connection with the Donnan equilibrium; *"the forces of secondary valence probably play a part here"* (p. 264). But that does not seem to embarrass J. Loeb seriously, and he then states that the problems of *gel formation or precipitation* (we would say coagulation or flocculation) *are not colloidal problems; they form part of a more general problem of solubility* (p. 284). Therefore, according to J. Loeb, there remain but two properties characteristic of the colloidal state: osmotic pressure and viscosity, just the ones we are inclined to consider as having nothing in common with the colloidal state, properly said. Few scientists acquainted with colloids will follow J. Loeb in these statements.

To demonstrate the identity of colloids and electrolytes in all these respects, Loeb asks the following question: "Are proteins maintained in watery solution by the same forces which determine the solubility of crystalloids in water, or, on the other hand, by electric double layers which hold in suspension droplets of oil or particles of collodion?" (p. 144). What he is really asking here is whether proteins may be considered as emulsions, or, *per analogiam,* whether it is correct to speak of "emulsoid sols" in opposition to "suspensoid sols."

Loeb then cites the experiments of M. C. Taggart on the charge of gas bubbles, of suspensions of collodion, and of emulsified oil droplets. Powis and Taggart have demonstrated that in these cases, the units behave exactly alike insofar as concerns the influence of electrolytes on their sedimentation. Loeb thus reaches the conclusion that proteins are kept in solution by action of the same forces as "crystalloids." What are these forces in proteins? Let us distinguish in the protein molecule those groups which have more affinity for water than the opposite. We will call them hydrophile. If the forces of the hydrophile groups prevail, the oily groups (reciprocal affinity) will be retained in the mass of the water. If the molecules are large and the oily groups few in number, it may happen that when these groups belonging to two neighboring molecules come into contact, the two molecules may adhere without materially diminishing the force with which the hydrophile groups are attached to the water (p. 151).

Without discussing the nature of these hydrophile groups, the question arises as to what force brings together the "two groups belonging to two adjacent molecules"? Why, when they touch, do they remain stuck together?

These physico-chemical conceptions will not satisfy anyone nowadays; they merely confirm that: "mit Wörten kann man trefflich streiten, mit Wörten kann man ein System bereiten." But these are *"Tempi passati."* Furthermore, Loeb cannot give explanation for the exceptions which he has brought out in the course of his researches: the special flocculating action of sulphate ions. ("The cause of this peculiar behavior remains to be established." p. 153.)

The experimental work of J. Loeb then warrants but two conclusions: *the physical properties of emulsoid colloids depend on the H ion concentration; among these properties, that of the electric charge of the micells permits us to glimpse the importance of the Donnan equilibrium in its appearance.*

These two conclusions are of prime importance; they can no longer be ignored. The credit for having drawn attention to them and having established them belongs to Sörensen and J. Loeb. These two conclusions of themselves make classics of the work of Sörensen and of J. Loeb.

But as for the balance, we consider it merely literature: the desire to subordinate the colloidal state to pure chemistry. It involves another conclusion: *in the absence of exact methods, in ignorance of the chemical constitution of raw materials, it is premature to desire to explain everything by one-sided generalized theories.* And if a working hypothesis is desired, it is the one generally recognized by all authors: *the colloidal state is intermediate between suspensions of solids dominated by physical laws, and true solutions, governed by chemical reactions; the same substance may, according to conditions, be in the colloidal state* (soaps in water, NaCl in benzene), *or in the soluble state* (NaCl in water, soaps in alcohol).

The laws governing colloidal phenomena cannot, therefore, be exclusively physical laws, nor solely the laws of classical chemistry. To the intermediate state there must correspond intermediate properties and intermediate laws.

The degree of dispersion controls these properties and these laws: the more dispersed a substance is, the more it approaches the state of true solutions, and the more closely its properties approximate chemical properties; with decrease in dispersion there reappears the preponderance of physical laws. That is why with variation in the degree of dispersion of the substances experimented with, we find ourselves confronted with so many chemical principles, and so many physical laws. And having in mind this importance of the degree of dispersion, we must be cautious against generalizing and building chemical or physical theories, which are always one-sided, and against being satisfied with one part of the truth, which is itself scattered amongst all.

Views of Malfitano.

In this physico-chemical controversy, Malfitano has taken an intermediate position; a position which is apparently intermediate, for as a matter of fact his views are purely chemical, as we shall see. Malfitano studied persistently and in great detail a single colloid: ferric hydroxide hydrosol. His desire to remain an orthodox chemist at any cost, led him, in the interpretation of his experimental facts, to a series of contradictions and embarrassing *impasses.*

Malfitano has certainly pointed out the complexity of colloids, when he notes the difficulty of explaining reactions occurring "even in the case of ferric hydroxide, although this appears the most simple of them all" (p. 238). "Furthermore," he says, "micells never consist of pure systems" (p. 553). That is why he is unwilling to accept either the physical view or the chemical view. "Scientists who follow too exclusively one or the other of these directions, must be forced to overlook part of the phenomena. The laws governing reactions between molecules cannot be readily carried over to very large particles almost within range of vision. And when micells have dimensions approaching those of ordinary molecules, it is hard to see how the conceptions of capillary chemistry can be applied to them" (p. 552). But at the same time he refuses to accept "too simple a picture, which represents colloids as granules which are chemically inert" (p. 552), and he holds that "not only do the phenomena of the colloidal state fail to subvert any of the theories of scientists who have founded chemistry, based on atoms and molecules, but they lend direct support to these theories" (p. 251).

Nevertheless, Malfitano does not accept the conclusions of the colloid-chemists. As to ferric hydroxide, he does not accept the explanation of Grimaux, de Reychler, and others, that there is involved a condensation with loss of water, "because it occurs on addition of water" (p. 237): he does not accept the analogy between these facts and those cited by Grimaux dealing with the transformation of glucose, when heated with concentrated hydrochloric acid, into a mass resembling dextrins but poorer in water. We may add that concentrated sugar solutions themselves exhibit certain behavior approximating the colloidal state of matter.

Malfitano believes that J. Duclaux has only destroyed "the simple theories developed apart from chemical ideas, but has not been able to replace them with a new theory in harmony with these ideas" (p. 248). He advances substantial arguments against the interpretations of Nicolardot and Wyrouboff, emphasizing the improbability of a cyclic structure in colloid micells. Neither does he approve the views of Grimaux, according to which the aggregation of molecules into micells follows the model of a process of esterification by which two alcohol molecules unite to form one molecule of ethyl oxide (ether), because, says Malfitano, "the bond between two chemical individuals as large and as heavy as visible micells, cannot be an atom of oxygen riding as it were tandem on both, since with the ethers where that is permissible, this bond is very fragile, especially in the presence of acids and water"; and "this bond is formed only with great difficulty, when molecules are involved like those of the sugars" (p. 237).

To exhibit in condensed fashion the strange chemism of a hydrosol, Malfitano states the properties of ferric hydroxide: "Heat to 100° C. a liquid containing one gram molecule per liter; . . . it becomes red, cloudy, and upon cooling it returns to its original condition. Dilute it 10 times before heating: it then becomes yellow, ochrous, opaque, and this modification will persist. Dilute this 50 times, and heat it. It becomes dark red like the concentrated solution; but on cooling, this dilute liquor remains heterogeneous. If we rise or fall in the scale of temperature, different modifications appear in the same order; there is a series of concentrations corresponding to each one of them. And still further: the solution of tenfold dilution will turn yellow if we take 15 minutes to heat it up to 100° C.; it becomes red if we reach that temperature in 5 minutes. Other things being equal, one of these modifications will take the place of the other, if the liquor heated is more or less aged. To the liquor which becomes red, add a little hydrochloric acid: according to its chlorine content, it will become yellow or brick red. The very diluted liquors become ocher-colored at ordinary temperature: one millionth of a gram molecule of phosphoric acid suffices to keep them limpid" (p. 513).

From the preceding it is perhaps natural to ask what is this chemical view of Malfitano. He has stated it "with the idea of reconciling views which are opposed, although they are inspired by a proper understanding of the facts" (p. 233). But at the same time he emphasizes, "contrary to the opinion most generally held, . . . an essential difference between physical and chemical phenomena" (p. 160). This consists in the following: "Matter in the micellular state in final analysis, differs from matter in the molecular state only by the continuousness and greater extent of its variations. No essential distinction exists between molecular and micells. But as micells are capable of being flocculated, they attain dimensions much greater than those of molecules. Sometimes the substance forming the micell changes with time, and without the occurrence of any direct reaction. The colloid is formed as has already been stated; but something more. The sols develop the most varied appearances. At first they resemble molecular solutions, but then become like liquids containing powders in suspension. I will therefore state that colloids represent a form in the evolution of matter between very different states. Any picture we wish to form of the micell, should take into consideration this evolutionary character" (pp. 551-552).

Concerning the mode of formation of the micell and all its successive modifications, Malfitano invokes chemical affinity. He admits fully that the micell is a mass of molecules; he agrees that a large number of facts "and those of great importance" (p. 212), are to be explained by the fixation, on this mass, of isolated ions whose number varies with their electric charge. But "electrolytes do not attach themselves to insoluble masses of matter to an unlimited extent, and not equally to all masses. Those which are fixed, being ionized, will account for the charge and consequently for the individuality of the micell. But in the presence of an excess of the same electrolytes in the intermicellular fluid, the electrolytes fixed will no longer be ionized, the charge will disappear, and flocculation or sedimentation will follow. Or still better (*sic!*) one can imagine that a single Fe can fix itself on the nucleus of $Fe(OH)_3$ molecules, the presence of other electrolytes, no matter what they are, will finally prevent the existence of this ion and will discharge the micells. Now in reasoning thus, we remove the question from the domain of ideas involving charge by contact to the domain involving ideas of affinity and valence. . . ." Nevertheless, apart from these arguments, Malfitano has been able to give no others for this "removal."

And then what a very curious affinity is that of Fe ions for a mass of $Fe(OH)_3$ molecules; and instead of a definite electrostatic idea (electric charge and its intensity) shall we prefer that of chemical "affinity," a term, a word? And when Malfitano tries to prop his view with experimental arguments, he encounters great logical difficulties. Let us take up some of the contradictions.

If we throw crystals of sublimed $FeCl_3$ into water, and there occurs a simple dispersion of matter, then, according to Malfitano, there should be a lowering of the temperature; on the contrary there is a rise. It is therefore more likely that the salt reacts with the water (p. 163). Parenthetically, we might remark that the phenomenon of syneresis is accompanied by the liberation of heat, but nevertheless no one ever dreams of considering it to be a chemical reaction, all the more so because coagulation is not accompanied by a consumption of heat, as is shown by the recent work of Gayda.

But let us continue. Malfitano admits combination by molecular addition between $FeCl_3$ and H_2O, and supposes that "there exist in these liquids multimolecular units of $FeCl_3$ and nH_2O" (p. 173). Then he invokes the formation of the compounds of Bechamps, having the formula $mFe_2O_3 . Fe_2Cl_6$ in which one molecule of ferric chloride attaches itself to a variable number of molecules of oxide. We hasten to say that in 1859 this might have passed unnoticed: the chemistry of valences was not yet very exact. Malfitano assumes the existence of compounds whose dehydration is not yet complete, of the following type

$$[Fe(OH)_3 \pm (H_2O)_n]^x . FeCl_3$$

and, further, this is one of a series of intermediate compounds, which it is easy to imagine on paper. "These complexes are not all molecules of complicated structure, but are molecules simply characterized by their mode of dissociation; they form in the liquid an ion which may be called complex" . . . for instance

$$\{[Fe(OH)_3 \pm (H_2O)_n]^x Fe\}^{+++}$$

which is balanced by Cl^- ions (pp. 181-182); and when support is sought in the work of Werner, we can imagine, according to Malfitano, that the complex ions or the chlorine is concealed; for example the ion

$$\{[Fe(OH)_3 \pm (H_2O)_n]^x FeCl\}^{++}$$

In all these flights of imagination and of pen, what is the *princeps movens* for the formation of these complicated complexes? What is the *why* of these combinations and scissions? It is surely not chemical "affinity" or even alchemy, for here the rules of valence are woefully mistreated. Neither is it because of electrical laws (electric charge and its intensity). What then? We find no reply to this question in the hypothesis of Malfitano. And, in fact, this search for a chemical formula means . . . so little: even with a crystalline substance, how often do we ignore this formula! Thus in the case of ferric hydroxide this formula is most certain: in 1901 Ruff thought that it was not $Fe_2(OH)_3$ but $(Fe_2O_3)_n(3H_2O)_m$. It is evident how this formula-play is facilitated by this first complication, and how many other formulas can be conceived of. And all this once more confirms the fact that there is conflict at frontiers; the greater the condensation of atoms, the larger the molecule, the more insufficient appear chemical laws; the size of the molecule then becomes a factor and warps the results. Just for this reason, in losing the broad point of view and remaining in the unfruitful valleys of chemistry, Malfitano could not see that his particular example, ferric hydroxide, was not completely amenable to physical laws, as it verged toward greater dispersion, toward true molecular solutions as compared with that imaginary standard, "colloids." That is why Malfitano's *general* line of argument is correct: "there is evident agreement between the theory of electric charge . . . in a general sense, and the theory of micellular complexes, which applies to the particular case studied here" (p. 244); but his special pleading is open to question, for it shows an obvious tendency to demand of chemistry things it is unable to do, especially nowadays. That is the reason Malfitano cannot explain *why* hydrochloric acid is less effective in proportion to the progress of the hydrolysis, a fact which he himself says "has never been observed in media acknowledged to be homogeneous"; why "this same acid has opposite effects, according to the conditions of its addition; it may either impede or facilitate hydrolysis; it acts on the micells either by deflocculating or peptizing them, or by flocculating them; it may increase or diminish their chlorine content" (p. 209); why the action of salts on ferric hydroxide is always to impede its hydrolysis, for his explanation, invoking double decomposition between ionized micell and added ions, or a particular action on the chlorine ion, is evidently without any *constitutional* basis.

The explanation of flocculation, which Malfitano regards as the formation of new complexes, and not from the electrostatic or kinetic point of view, is one of the most edifying, with regard to complexity, involved in this problem.

"Micells in flocculating do not necessarily change in composition . . . , in the group the Fe/Cl ratio changes but little if at all, and in any event in an irregular fashion" (p. 186). Where then are we to find equimolecular proportions?

Here are a series of complexes where the negation of chemical rules clearly appears:

$$\{[Fe(OH)_3 \pm (H_2O)_n] \times Fe\}^{+++} Cl^{---}$$
$$\{[Fe(OH)_3 \pm (H_2O)_n] \times FeCl\}^{++} Cl^{--}$$
$$\{[Fe(OH)_3 \pm (H_2O)_n] \times FeCl_2\}^{+} Cl^{-}$$
$$\{[Fe(OH)_3 \pm (H_2O)_n] \times FeCl_3\}$$

. . . .

$$\{[Fe(OH)_3 \pm (H_2O)_n] \times Fe(OH)_2\}^{++} Cl^{--}, \text{ etc.}$$

In all these deductions, Malfitano rests on his patient, meticulous and rigorous experiments. Do they, however, permit the conclusion that the micell is ionized? Upon reflection, Malfitano himself says no, thus showing himself to be a very cautious and prudent investigator: "this might lead us to think that, by the methods here employed (electric conductivity, cryoscopy, ultrafiltration, osmotic pressure) we come directly to a determination of the true physical constants of the micells, so that a way would be opened to the molecular composition. The mass, the velocity, the degree of electrolytic dissociation of the micells seem to me to be too variable for determination by these indirect methods" (p. 547).

Regarding osmotic pressure, Malfitano emphasizes that "the membrane is altered, it does not remain unchanged when impregnated with a colloid. When used to filter solutions freshly prepared from ferric chloride, the membrane remains entirely uncolored. The alteration of the membrane is occult; using Perrin's method of electric osmosis, I was able to prove that the colorless membranes have a negative charge, and that after impregnation their charge becomes positive. If an impregnated membrane is employed in a new experiment, from the outset the drops of liquid to come through will be red" (p. 524). This is, besides, a potent argument against measurement of the real osmotic pressures of colloids, suggested from time to time; it explains incongruities in physical constants like the following:

	Fe	Cl	C at 18° C.	Δ
Ferric hydroxide hydrosol (dark red)..	0.032	0.093	0.0216	0.270
The same after ultrafiltration...........	0.008	0.089	0.0226	0.280

We will not stop to consider other hypotheses of Malfitano, such as the distinction, fundamental for him, between crystalline and amorphous substances, and between flocculation and crystallization, questions which the work of Zsigmondy, Scherrer and others has rendered moot.

To sum up, Malfitano's views again prove the danger of any onesidedness in theories regarding the mechanism of the formation and stability of colloids. It may perchance prevent framers of theories from falling into the error of forgetting, while they are generalizing from special cases, to remember that before comparing such cases with the properties of molecularly dispersed substances and suspensions, they must above all fix their place in the scale of dispersion.

Views of Zsigmondy.

Quite recently a similar theory was formulated by Zsigmondy, having perhaps a slight leaning toward the purely mechanical concept.

Starting from the researches of Werner and Mecklenburg, he considers at the outset that it is possible to explain certain properties of colloids by the volume and also the form of micells. We have on several occasions pointed out the deliberate neglect, by Zsigmondy, of capillary forces, a fact which has been commented on by several authors. Granting that surface tension and viscosity, beyond doubt, play a capital part in the formation of colloids, certain conclusions of Zsigmondy regarding the form of micells appear hypothetical to us. We will take this up later on. We allow that Mecklenburg's researches showed a difference between the properties of the two hydrosols of stannic acid, α and β, and the coincidence between these differences and the degree of dispersion. But does it follow that the degree of dispersion is the only dominant factor? *Post hoc ergo propter hoc* is not always a perfect syllogism. And is it also proven, as Zsigmondy would have it, that the color of a hydrosol depends on the separation of the primary and secondary particles or micells?

In any event, in a general way, Zsigmondy's ideas strongly support the physical idea of the colloidal state, and we cannot do better than to quote to adherents of the chemical theories, the following statement of Zsigmondy:

"We are accustomed, in chemistry, to ask investigators who speak of the existence of a chemical compound, to give proofs of its existence, its makeup, and its detailed description."

Physical Views.

Opposed to these one-sided chemical conceptions are the physical theories. Even Selmi,* the real founder of colloid science, had strongly emphasized that we are faced by an altogether peculiar state of matter which chemical laws are far from able to explain. Let us quote several passages from his works which point this out.

"The solid particles in question, bathed in a liquid, can absorb, swell, subdivide into a variety of membranes or pellicles, which are transparent, separated from one another, or attached to one another to form a circular reticulum . . . scattered uniformly in the vehicle, rendering it gluey, or without changing its initial viscosity . . . , thus simulating a true solution, although in reality it is only an *extension,* a *suspension* of particles, and not of molecules, in a liquid medium. In other cases the solid separates in soft, opaque globules, which is why the liquid is no longer transparent and forms an emulsion" (p. 37, *Dissertazione intorno all'azione di contatto*).

"The term *coagulation* does not mean a change of state of a compound, but a molecular disturbance (turbamento) . . . we distinguish a precipitated albuminoid substance from a coagulated albuminoid, by the addition of a substance which produces a change of state, and we have either a re-solution or else a totally insoluble substance." (Annali Majocchi, Vol. 6, p. 22.)

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* English translations of some of Selmi's papers were published by the Colloid Committee of the British Association for the Advancement of Science in 1925. J. A.

Francesco Selmi has also given us a clear sketch of the phenomena of dyeing. He said:

"We are not of the opinion that dyestuffs *combine chemically* with textile fibers. Mineral or vegetable carbon will decolorize liquids containing dyes in solution or pseudo-solution . . . without mutual combination between the molecules, because the carbon preserves its initial appearance and the dye may be liberated intact if we agitate with stronger solvents than simply water or alcohol. . . .

. . . Chemical affinity is not involved . . . the phenomenon has its origin in the adhesion to which the dye particles are subjected by the surface of the granules or particles (polviscolo) of carbon." (Principii elementari de chimica organica, Torino, 1851.)

Subsequent to Selmi, Graham emphasized the fact that the colloidal state is intermediate between molecular-chemical dispersion and mechanical subdivision, observing that between these states there should exist a series of transitory degrees. But this physical conception was especially reinforced by the work of Bredig. This German investigator gave us a theory of flocculation which may be considered experimentally proven, as we shall see below.

Bredig took the following view of flocculation: "A diminution of surface of electro-capillary origin, which occurs more rapidly when adsorption causes a further lowering of the potential difference, and, in consequence, a greater increase of surface tension against the surrounding medium. And as this surface tension should be a maximum at Hardy's isoelectric point, my conception of coagulation as a Lippmann phenomenon explains at the same time Hardy's observation that it is just the isoelectric colloids or suspensions which are the most unstable and coagulate, that is diminish their surface most rapidly."

Bredig's views were taken up by Cotton and Mouton, then by Perrin, and, after having undergone a mathematical review by Smoluchowski, were experimentally confirmed by Zsigmondy. It is invariably in the conception of flocculation that the physical theory shows up best, stressing the difference between this phenomenon and chemical precipitation. Here are the ideas of Perrin and Smoluchowski on this subject.

To make a beginning, Smoluchowski assumes there is an alteration in the spheres of attraction between micells following the introduction of electrolytes or colloids: this sphere of micellular attraction is in close relation with the electrical double layer of each micell; when because of Brownian motion a micell penetrates into this sphere of attraction, it loses its movement and unites with the micell in question. The nature and intensity of this micellular sphere of attraction depends on the concentration of the electrolytes and the change in charge that they cause. Zsigmondy has shown that the radius of the sphere of attraction for colloidal gold equals 2 to 3 times the micellular radius.

Smoluchowski then considers whether the mechanism of flocculation is identical with the kinetics of chemical reactions, and whether it does not lead toward an explanation of chemical reactions. Smoluchowski's answer is a direct negative. The Polish physicist observes that with chemical reactions mere contact between the molecules is not enough; it is essential that they be quite characteristic; chemical reactions depend on the laws of valence, while in flocculation we see an indefinite agglomeration; and many other arguments. In fact if we use the theory, established and confirmed for colloids, we obtain values inconsistent with the velocity of chemical reactions.

It would be easy for us to continue the experimental demonstration of this difference between colloidal reactions and the stoichiometric laws of classical chemistry. We have given, and many a time emphasized them in discussing the chemical views.

Let us take them up again and complete them by several general examples.

The solution of electrolytes and of colloids had been minutely studied by Selmi. We quote several passages from his works which show the difference between these two phenomena.

"When we dissolve the crystalline salt (Na_2SO_4) in an equal weight of water at + 50° C., pour the solution into a glass tube, cork it up hermetically and then cool the solution to 0° C., the salt does not crystallize; but it crystallizes immediately when the cork is withdrawn. . . ."

"If a hot solution is poured into a glass flask having a long straight neck into which a thermometer is introduced, if the neck is hermetically sealed; and if during the cooling to 0° C. marks are made showing where the liquid is every 5° all the way down to 5° C.; and if the flask is now placed in iced water and opened; then the salt begins to crystallize, the temperature rises to + 17.5 to 18° C., and the volume of the solution increases so that it reaches the mark it had at 43° C. If the flask is plunged into iced water to speed the chilling, the volume of the mass continues to increase despite the chilling, so that when the temperature reaches 0° C. the mass occupies the same volume that the liquid occupied at + 50° C. However on heating the solution gradually so as to dissolve the salt, the thermometer rises and the liquid falls."

Selmi then considers solution, by analogy with gases, as a dispersion of solid in liquid, without having recourse to a special affinity of combination, which shows none of the characteristic features of true chemical affinity. "This dispersion goes down to particles so fine and uniformly distributed that it is really an expansion of dispersed molecules, comparable to that of vapors in space . . . it is *a vaporization of a solid in a liquid.*"

The liquids studied above are distinguished from true solutions for the following reasons: (1) because they do not lower the temperature of the solvent when dispersing, nor do they raise it in precipitating or crystallizing;* (2) because these phenomena are not accompanied by changes of volume; and finally (3) because the liquids obtained permit the separation of their solid matter under the influence of minute traces of indifferent salts having no chemical affinity with them, and acting solely by modification of the properties of expansion of the particles.

This is why they are only *pseudo-solutions,* despite their superficial resemblance to true solutions.

More recently Malfitano has also studied solution with the ultramicroscope. After minute observations, he considers that the difference between the two sorts of modifications is evident: The crystal merely "diminishes in volume, and nothing is seen of the fragments which must however detach themselves from its surface.† This is solution. The pseudo-crystal, on the contrary, disperses completely and at once into perceptible and uniform granules which remain coherent." The same observations were made by Fouard on starch and on dextrin, and he called this phenomenon *disaggregation* and not solution.

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* Refined measurements show that this is not so. See paper by Mathews and Browne, this volume, p. 450. J. A.

† Crystals of sodium citrate show the detachment of colloidal aggregates when going into solution. Alexander and Bullowa, *Arch. of Pediatrics,* 1910.

Still more marked differences are found in the *precipitation of electrolytes* and the *flocculation of colloids.*[*]

In the first place there are the two well-known disturbing characteristics of the flocculation of hydrosols: their *reversibility* and their *periodicity.*

Here is a typical example of *periodic* flocculation of a platinum hydrosol by ferric chloride, according to Buxton and Teague.

Amount of $FeCl_3$ Added	Effect	Electric Charge
0.0208	No flocculation	Anodic
0.0833	Complete flocculation	Amphoteric
0.3333	No flocculation	Cathodic
16.33	Complete flocculation	Amphoteric

The *reversibility* of a colloidal flocculation has been often studied, and the method of Kuzel for the preparation of numerous colloids is based just on this reversibility of a flocculate when formed. In 1899 von Hahn, and quite some time previously, Senderens, described the preparation of soluble antimonic acid, on the basis of this reversibility.

"When brought into contact with water after having been desiccated in air, antimony hydrate $Sb_2O_5 . 6H_2O$ hardly dissolves. This is not the case with recently precipitated hydrate, which indeed dissolves even in the cold in considerable quantity, provided however that every trace of mineral acid, which prevents solution, is removed by washing with cold water."

Let us recall a few other facts which support the differentiation between flocculation and precipitation. In the first place numerous examples demonstrate the action of traces of various foreign substances, without following the laws of equimolecular proportions. Graham has given us a great number of cases in point: that of alumina which was "coagulated by a few drops of well water and which moreover could not be poured from one vessel to another without gelatinizing" (p. 175); "the presence of carbonate of lime in water has been found to be incompatible with the coexistence of soluble silicic acid, unless the proportion of this latter has been reduced to about 1 part in 10,000 parts of water" (p. 123); traces of carbonic acid gelatinize silicic acid (p. 170), but at the same time the hydrosol will stand large amounts of strong mineral acids, alcohol, etc., without being changed. . . . (p. 123).

But these facts, as well as the possibility of replacing sulphuric acid in a sulphosol of silicic acid by water or alcohol and thus reproducing exactly the original hydrogel (p. 125); of introducing fixed oils into the etherogel of this same silicic acid, these elicited from Graham merely the following reflection: "There seems to be formed no permanent combination between sulphuric and silicic acid under these circumstances."

Apart from this absence of chemical "affinity," the researches of Bechhold and above all those of Freundlich have developed troublesome facts impossible to reconcile with actual chemical views. We have already pointed out the importance of *rapidity of mixing,* as well as the *order of addition* of two flocculating liquids in producing change of state. In fact we have said that the *infinitesimal quantity* of the flocculating substance has nothing to do with equimolecular proportions of chemical reaction. Bechhold found that in the coagulation of albumin by heat in the presence of electrolytes, it is especially the first very minute portions which act mainly, and the addition of larger quantities has little effect on the temperature of coagulation. The following table shows this:

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[*] See paper by A. Lottermoser, this volume, p. 670. J. A.

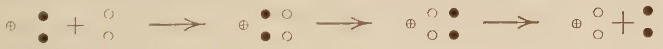
Salts	Temperature of Coagulation in Concentrations of				
	0	0.01 N	0.02 N	0.04 N	0.05 N
	° C.	° C.	° C.	° C.	° C.
NaSCN	60.3	68.0	69.7	71.6	72.5
Na_2SO_4	60.3	66.7	68.0	69.1	69.7
NaCl	60.3	63.1	65.7	67.2	67.9
$NaC_2H_3O_2$	60.3	66.9	69.2	71.5	72.1

Graham and later Jordis pointed out the extreme sensibility of certain hydrosols: the quantity of carbon dioxide diffusing through a rubber stopper suffices to coagulate silicic acid hydrosol. This explains the "spontaneous" coagulation of colloids, referred to from time to time, which Zsigmondy demonstrated to be incorrect, by preserving for years a gold hydrosol suitably prepared and free from impurities, and kept in a receptacle away from light. Arrhenius pointed out the neutralizing action on colloids of the alkalis from glass. Zsigmondy showed the extreme sensitiveness of the purple of Cassius.

In short all properties of colloids and every colloidal reaction present peculiar features due to the intermediate position of the degree of dispersion of this state of matter. And if we deviate ever so little toward greater dispersion, we suddenly see chemical reactions beginning to dominate; if toward lesser dispersion we discover physical laws regulating solids and liquids.

In the former case, the example most studied is that of molecular aggregations. Next to Menschutkin and Werner, we are especially indebted to Pfeiffer for interesting work on molecular complexes.*

How was this view arrived at? In the first place because of the insufficiency of the theory of valences. With the increasing number of compounds obtained, we were more and more often obliged to have recourse to "exceptions" and to consider the same element under the aspect of modified valences. There are the examples of nitrogen, of phosphorus, and above all of cobalt, of molybdenum, etc., . . . and even of carbon. On reflection we are faced with the necessity that atoms must approach each other in order to effect a chemical reaction; this approach must be within certain limits in order that the *"forces of attraction"* be sufficient. Therefore the first phase of a reaction will be an approach of molecules. The idea recently championed by Reddelein was already expressed by Kékulé in 1858 and by Van't Hoff in 1881; the following diagram illustrates it sufficiently:



$MgBr_2$ Cl_2
Phase I Phase II Phase III Phase IV

It is evident that Phase II may be considered to be a molecular compound, obviously unsuitable in this case, but which in others might have sufficient stability. The existence of these compounds has been shown in several reactions of halogenization and substitution (of halogens, hydroxyl, etc.). Wroczynski and Guyes were able to demonstrate that aniline and ethyl acetate give intermediate compounds when the reaction takes place at low temperature, but on heating these intermediate compounds give ethylaniline. Schniedlin and Lang have shown the frequency of molecular complexes in condensation reactions under the influence of concentrated sulphuric acid. We need not multiply examples, but simply note that the reality of these complexes is one of the arguments in favor of the theories of catalysis which have long assumed the formation, in this phenomenon, of very unstable intermediate bodies.

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* We say molecular complexes and not "combinations"; this seems more logical in order to distinguish them from true chemical compounds.

It seems then that there is no doubt as to the existence of molecular complexes. But this is at the same time an argument in favor of the insufficiency of the rules and the laws of the traditional chemistry of valences, of the necessity of admitting that there are other reactions than those of substitution and of double decomposition. This is a logical argument; but the properties of these compounds constitute another argument, an experimental one, in favor of this point of view. Let us examine into these properties.

Among the increasing number of molecular complexes, let us choose several striking examples.

Cobaltic complexes have especial interest in this connection. Cobaltic salts of the type CoX_3 (X being a monovalent radicle), can take on as many as six molecules of ammonia; but there are compounds having only five, four or three of these molecules. They are called cobaltic hexamines, pentamines, tetramines and triamines. Of all these compounds, according to Pfeiffer, the triamine is not at all ionized in aqueous solution, but forms a "neutral ion" ($CoX_3 . 3NH_3$). This fact should be emphasized because it shows that there is no need of assuming an ionization of a complex, in order that it should react with other substances; all the more reason why colloids need not be ionized. Just as with cobaltic compounds, those of chromium, of iridium, of rhodium, etc., need not in certain cases show any sign of dissociation.

Take the example of the organo-metallic complexes. We know that with these complexes the chemical reactions characteristic of each element introduced are lacking; we say that in them the element is dissimulated. On measuring the electrical conductivity of certain organic compounds, we found that in certain cases the metal introduced in no way changed the degree of dissociation of the substance. Take the example of milk: introduce into this liquid 1 per cent of metallic iodine and measure the conductivity: it will hardly be changed.

Pure milk	*Iodized milk, 1 per cent*
86.0×10^{-4} at 25° C.	90.0×10^{-4}

Compare this change with that obtained by dissolving metallic iodine in distilled water.

Distilled water	*Iodized water (1 to 3600)*
0.06×10^{-4}	7.3×10^{-4}

Without considering the concentration, the conductivities are about as 1 to 20.

The same is the case with other organo-metallic products. We measured the electrical conductivity of 1 per cent arsenobenzene, and of 1 per cent galyl; the former was 72.4×10^{-4} at 25° C., the latter 56.6×10^{-4}. Comparing this with the conductivity of an electrolyte of the same concentration (1 per cent NaCl at 25° $= 129 \times 10^{-4}$), and remembering their high arsenic content, we might say that these substances are very slightly ionized. Another common characteristic they have, and one which we have discovered in typical colloids, is the increase of their conductivity by dilution. The following are the results for arsenobenzene:

2 per cent	118.1×10^{-4}
1 per cent	72.4×10^{-4}
0.5 per cent	42.0×10^{-4}

All these peculiarities justify us in regarding organo-metallic and other complexes as transition bodies between electrolytes and colloids. Is it then possible or necessary that colloids should obey the laws of valence? Evidently not, for it is just because of the impossibility of applying these laws to them, that we have been forced to investigate, and if we may say so, to explain the mechanism of their formation and their properties.

So that the Chinese puzzle invented by Werner and complicated by his adepts is in no wise necessary: it is superfluous and paralogical! The play of secondary valences, internal and otherwise, will never explain the intermediate properties of molecular complexes, and this is the only question that interests us. The explanations of Werner and of Pfeiffer become more nebulous as they proceed, and these authors are obliged to say "that it is very difficult to decide which, among the formulas possible to imagine, is the true one, for all of them are sufficient to explain everything." (p. 112.)

Pfeiffer's research on the polypeptides showed that various neutral salts, in their action on these substances, behaved exactly the same as with natural proteins, so far as concerns their solubility, their separation, adsorption, lowering of the setting point, etc. (pp. 119-124). Thus the Hofmeister series is once more reëstablished, and the view prematurely advanced by J. Loeb is refuted by the classic chemists themselves. Once more we ask, how can we invoke, in this case, the chemical affinity of valence, etc., . . . ?

This chemistry of molecular complexes is therefore very complex. Under the impulse of the work of Jörgenson and of Werner, there has been produced an abundance as regular as that of organic chemistry. But as Job recently remarked "even the most perfect complexes are much nearer a state of mobile equilibrium than are most organic compounds. . . . The properties of these bodies are often imperfectly known, their very composition is sometimes uncertain, and their constitution hypothetical. And we suspect that Werner's formulas are nothing but an ingenious method of cataloging the known species, without corresponding to their real properties." This is why Job and Urbain, in subjecting Werner's views to sharp criticism, have often reached total disagreement.

As a matter of fact the whole question is quite simple if we will but quit for a moment the more and more confined valleys of chemistry, and climb a peak in order to take a bird's-eye view of the whole: we will easily get our bearings.

To sum up: organic compounds are the first bond uniting ionized substances and colloids; they obey but a part of the laws of pure chemistry. Moreover, chemical forces themselves have begun to receive an explanation, thanks to recent work of physicists on atomic structure.

The striking progress in the science of physics has proven the insufficiency of atomic views. Cathode rays, made up of negative electrons, whose weight is about one two thousandth that of the hydrogen atom, were the first example of the divisibility of atoms. By measuring the direction and extent of the deviation of cathode rays, we were able to determine the size and weight of other electrically charged material particles. The discovery of radioactive substances was still further proof.

We know that radium gives off rapidly helium and emanation, and that it finally changes into lead. The transmutation of the alchemists has become an accomplished fact;* isotopes were discovered. Finally research in the optical properties of atoms revealed other facts of capital importance in clearing up the structure of the atom. Heat, electricity and other forces cause atoms to emit radiations; these radiations are distinguished by their wave lengths; the quantum law (relation between energy and radiation), makes it possible to determine the nature of these radiations and the nature of the changes taking place in the atom.

All this has led to a better idea of atomic structure; the microcosm appears to be a duplicate of the macrocosm; the atom is like a solar system: electrons revolve about a positive nucleus; their rapid rotation prevents the electrons from falling into it. The lightest atom, that of hydrogen, is the simplest in structure. Besides, observations seem to indicate that the properties of atoms depend solely upon the exterior electrons. Chemical reactions seem to be modifications of electronic motion and of its intensity. Chemical affinity becomes electric affinity.

Consideration of the work of Bohr, Werner, Langmuir, Kossel, Langevin, Lewis, and others, permits us to draw the following conclusion: matter seems to be an aggregation of particles of electricity having opposite signs, and it therefore seems beyond doubt that chemical affinity is of an electrical nature. When atoms are combined into molecules, we must attribute an essential rôle to electrostatic action (Coulomb's law). The idea of valence, insufficient in the case of complexes (Werner), and of hydrocarbons with double bonds, begins to become comprehensible by electrostatic laws, as does also the idea of affinity.

But all this (theory of Kossel, Lewis, Langmuir, etc.) still does not give a solution to this problem of affinity; it does not explain the *variation* in atomicity (Mn may have 2, 3, 4, 6 or 7 valences); it does not permit us to foresee the changes in characteristic properties (the substitution of H by Cl and Fl, in acetic acid increases its acidity), etc. . . .

It is the beginning of an explanation as well as of harmonizing the discrepancies observed in the properties of certain chemical compounds, especially molecular complexes and organo-metallic compounds, and besides of the nature of chemical affinity. For this explanation we must thank progress in physics; and it confirms the idea long ago expressed by Liebig: "die chemische Verbindung ist aber ein, und sicher nicht der einzige Effekt der chemischen Affinität" (chemical combination, however, is one, and not the only consequence of chemical affinity). It shows once again that the efforts of "pure" chemists to express a substance alphabetically and numerically gives no explanation of its properties or of its structure—the formula $CaCO_3$ does not inform us as to the colors of mountains, the symbol C does not say why a diamond may be blue, black or colorless. It compels us to break away from the habit of establishing air-tight divisions between states of matter, and simplifies the laws governing matter.

Returning to the colloidal state, we are then enabled to weigh and place it well in its position, and realizing its intermediate position, to attribute to it properties which are sometimes physical, sometimes chemical, and sometimes intermediate, according to its degree of dispersion.

Finally, McBain has pointed out this intermediate position of colloids and of the intermediate state between solutions and suspensions. Further consideration permits us to prepare a schematic table showing the different degrees of dispersion of matter and the modifications and properties resulting therefrom.

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* At the Aug., 1924, meeting of the British Association for the Advancement of Science, Sir Ernest Rutherford described how he had succeeded in bringing about the transmutation of several other elements through the aid of α particles shot out from radium. J. A.

Degrees of Dispersion	Osmotic Pressure	Diffusion	Electrical Conductivity	Electric Charge	Optical Heterogeneity
A. *Solutions*					
Electrolytes	+ + +	+ + +	+ + +	+ or —	0
Non-electrolytes	+ + +	+ + +	0	0	0
Molecular complexes.	?	?	0	+ or —	?
Hemi-colloids	+	+	+	+ or —	+
B. *Colloids*					
Lyophile	0	0	0	+ or —	+ +
Lyophobe	0	0	0	—	+ + +
C. *Suspensions*	0	0	0	—	+ + + +

In order to place ourselves readily in these different degrees of dispersion, we might use the following terminology:

Ionoids = Electrolytes (crystalline — KCl, or amorphous — $HgCl_2$).
Moloids = Ampholytes (sugars, organic liquids, etc.).
Moleculoids = Molecular complexes (luteo-cobaltic, etc. . . . organo-metallic compounds).
Electroids = Hemicolloids (colloidal electrolytes of McBain, soaps, etc., dyes, ferric hydroxid, etc.).
Micelloids = Colloids.
Dispersoids = Suspensions (microscopic or macroscopic).

To sum up this long review, and without fear of repetition, it is clearly evident that the colloidal state is an intermediate one between suspensions of solids governed by physical laws, and true solutions governed by chemical reactions: the same substance may appear, according to conditions, either in the colloidal state (soaps in water, $NaCl$ in benzene) or in the molecular state ($NaCl$ in water, soaps in alcohol).

Therefore, the laws governing colloidal phenomena cannot be exclusively those of physics nor simply those of classical chemistry. To the intermediate state there should correspond intermediate properties and intermediate laws.

The degree of dispersion is the arbiter of these properties and these laws: the more a substance is dispersed and the more it approaches the state of solution, the closer its properties will be to chemical properties; with decreasing dispersion physical laws again dominate. That is why, *according to the degree of dispersion of the substance under consideration, we are sometimes confronted by chemical laws, and sometimes by physical laws,* and bearing in mind this importance of the degree of dispersion, we must guard against generalization and advancing chemical or physical theories, which are ever one-sided and have but part of the truth, which is, itself, among them.

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Adsorption and its Significance

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I. The Most Important Characteristics of Adsorption Phenomena

The question, "what is adsorption?" cannot yet be unequivocally answered. The concept of adsorption developed from the observation that very porous substances, as charcoal, kieselgur, etc., are able to hold gases or dissolved substances rather loosely. To decide in any given case whether or not we are dealing with an adsorption, we proceed empirically about as follows: Suppose a finely divided or very porous substance, when added to a true solution of a non-colloidal, non-dissociated substance, reduces its concentration to a marked extent. We first of all test whether this reduction of concentration takes place rapidly; in the case of adsorption it is almost completed within 10 to 20 minutes. We then investigate whether the endpoint corresponds to an equilibrium. It should be possible to remove the adsorbed substances again by means of lixiviation.

With real adsorption we are dealing with true equilibria; it makes no difference whether we come to these equilibrium concentrations from higher or lower concentration levels, we always arrive at the same endpoint.

Of course we can recognize this removability of the adsorbed material only if the reduction in concentration is not so great that practically none of the dissolved material remains in the solution. The very concept of the equilibrium presupposes that the liquid used for washing must contain less of the substance than the solution in which the equilibrium exists. If the latter shows nothing on analysis, this will naturally be the case in the lixiviating solution.

If we designate by "a," the amount of substance which is adsorbed by 1 gram of the solid porous mass, *the adsorbent,* and by "c" the amount left in solution when equilibrium is reached, we find that the following equation holds with considerable accuracy

$$a = \alpha c^{1/n} \tag{1}$$

In this equation α and $1/n$ are constants, and α may have all possible values, whereas $1/n$ is usually smaller than 1 and lies between 0.1 and 0.7. The equation is merely empirical and undoubtedly only approximately correct. It expresses, however, the essentials of the adsorption equilibrium, namely, that with increasing concentrations in the initial solution there will always be relatively a less percentage adsorbed. It will be referred to in what follows as the ADSORPTION ISOTHERM. As a final characteristic let it be remarked, that in most cases the temperature factor is not large and as a rule the adsorbed quantity decreases with a rise in temperature, often only 1 per cent with a temperature increase of 30 to 40°.

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* Translated by Dr. Paul Mahler, New York.

The exponent $1/n$ on the other hand increases with the temperature and with higher temperatures approaches the value 1.

What has been mentioned above can be applied without further comment to the adsorption of gases by solids. The equilibrium pressure is generally used in the adsorption isotherm instead of the equilibrium concentration. With gases we observe a marked increase in adsorption with a drop in temperature. Charcoal adsorbs nitrogen, oxygen, etc., very powerfully at the temperature of liquid air, while at ordinary temperatures these gases are only slightly adsorbed. According to Dewar's method, in order to obtain a high vacuum there is used for adsorption carbon which has been cooled by liquid air. There are also instances of adsorption by smooth surfaces, of methane by mica plates,[3] of toluol vapors by glass plates,[4] etc. This clearly indicates that we are really dealing with a fixation of the adsorbed substance at the surface of the solid, furthermore the fact that the equilibria are reached so rapidly and are reversible. Since diffusion into a solid requires a long time, it is therefore not probable that the adsorbed molecules penetrate to any great extent into the solid.

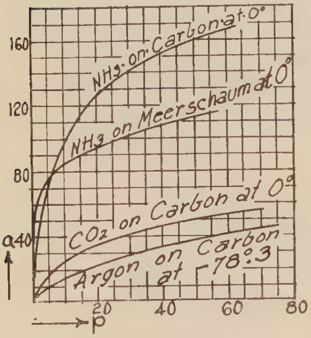


FIG. 1a.

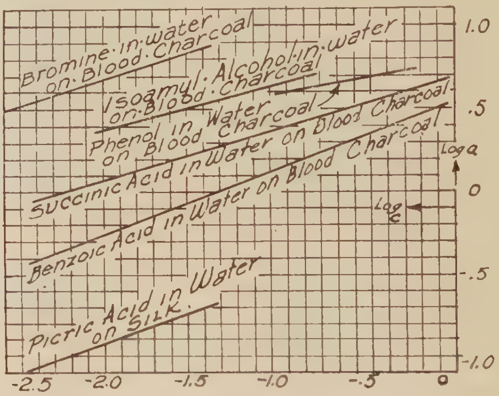


FIG. 2a.

In Figs. 1a and 2a are reproduced adsorption isotherms for several dissolved substances and gases. The abscissa are the concentrations "c," or pressures "p"; the ordinates, the adsorbed quantity "a"; the concentrations are expressed in equivalents per *liter,* the pressures in cm. of mercury; the adsorbed mass of dissolved substance in milli-equivalents per gram of adsorbent, for gases in cc. (calculated to 0° and atmospheric pressure) per gram of adsorbent.

If we take the logarithms of both sides of equation 1, we obtain

$$\log a = \log \alpha + 1/n \,.\, \log c, \qquad (2)$$

i.e., the equation of a straight line. For this reason we have reproduced in Figs. 1b and 2b several adsorption isotherms as logarithmic diagrams, in order to show that they do actually conform to the equation of straight lines.

Our purview is too narrow if we consider only the adsorption of gases and dissolved substances by solid surfaces. There are also phenomena at other interfaces which we are forced to regard as adsorptions. For instance, if a stream of mercury in fine drops is allowed to flow through a solution of a dyestuff such as New Fuchsine, picric acid, etc., and care is taken that the solution through which the stream of mercury has passed does not immediately mix with the rest of the solution, at the place where the mercury drops combine, a diminution in the concentration of the solution will be observed.[5] This can take place only if the mercury is divided into small droplets. The adsorption takes place quickly and is reversible, the adsorbed mass increases with the concentration of the solution, relatively more being adsorbed with low concentrations than with higher concentrations; hence a marked similarity to the previously mentioned experiments.

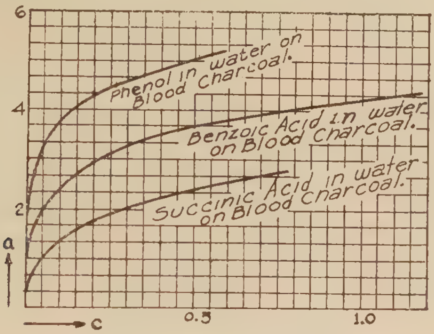


Fig. 1b.

The same thing occurs if fine air bells are bubbled through an aqueous solution of nonylic acid, amyl alcohol, etc., care again being taken that the liquid at the point where the bubbles burst does not mix with the rest of the solution.[6] The solution likewise becomes poorer in dissolved substance and this cannot be interpreted otherwise than that the concentration at the surface of the air bubbles is greater than in the rest of the liquid, just as was the case with the mercury droplets.

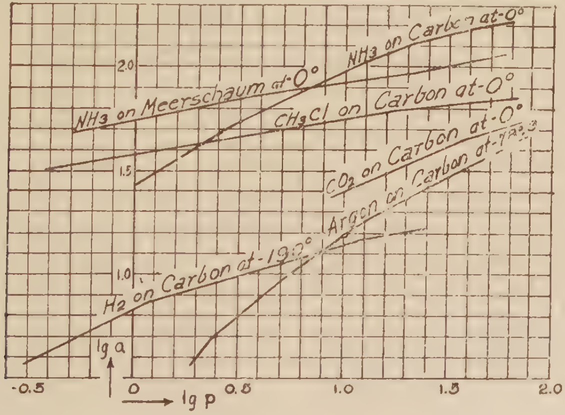


Fig. 2b.

The above mentioned phenomena can be traced back to the Second Principle of Thermodynamics. Gibbs[7] was the first to point out that a gas is condensed at the surface of a liquid, if with increasing pressure it lowers the surface tension of the liquid. Following his deductions, we can formulate in general the principle, *that if a dissolved substance, with increasing concentration, lowers the surface tension of a liquid relative to the gaseous space above or to a second liquid phase, then it will be concentrated at the interface.* This relation for a solution can be expressed in the form of

$$a = -c \cdot \frac{d\sigma}{dc} \cdot \frac{dc}{dp} \tag{3}$$

where a represents the excess of dissolved substance which is present per square centimeter of the surface, c, the concentration of the solution at equilibrium, p, the osmotic pressure of the solution, σ, the surface tension. If Van't Hoff's Laws hold for the solution, we can substitute

$$\frac{dc}{dp} = \frac{1}{RT}$$

and hence equation (3) becomes

$$a = \frac{-c}{RT} \cdot \frac{d\sigma}{dc} \tag{3a}$$

Equation 3a also holds for the adsorption of a gas if we substitute for the concentration c, the equilibrium pressure p.

The value a is very closely proportional to the already defined quantity a. If we regard this concentration of the dissolved substance at the interface is an adsorption, then from 3a we may postulate the following principle: *"The quantity adsorbed increases in proportion as the surface tension of the solution becomes diminished by increasing concentration."* In like manner we must expect that the quantity of solute held at the surface will diminish, if the solute increases the surface tension. This relation will be designated in what follows as *Gibbs' Adsorption Law.*

The above mentioned examples of adsorption on mercury droplets and air bubbles harmonize essentially with this theory. Patrick[5] was able to show that the surface tension of mercury was lowered by the following substances in the order, new fuchsine <, picric acid < salicylic acid < mercurous sulphate, which is the same order as for adsorption. New Fuchsine is the least adsorbed and mercurous sulphate the most. The concentration of materials at the surface of air bubbles could only be observed with those substances which were able to lower the surface tension markedly. It is true that we cannot verify this relation quantitatively. Experiments in that direction proved, however, that the order of the magnitudes was in agreement with the theory.

It is safe to assume that adsorption in general, including adsorption at solid interfaces, depends upon the surface concentration pointed out by Gibbs. Heretofore it was not possible to prove this relation definitely. There is no method whereby we can measure the surface tension of a solid with respect to a gas, or its interfacial tension with respect to a solution; and this is necessary in order to verify equation 3a. Nevertheless a large number of observations indicate qualitatively that a great number of adsorptions at solid interfaces can be regarded as surface concentrations. Of all these we shall discuss only one, the so-called Traube's Law for liquid as well as solid interfaces. This law manifests itself upon measuring the surface tensions of aqueous solutions of organic substances, which, generally speaking, markedly lower the surface tension of water; and this lowering takes place in regular order as we ascend the homologous series. Figure 3 shows this relation for the aqueous solutions of fatty acids; the concentrations are expressed in moles per liter and the surface tensions in dynes/cm. One can see, that with a given concentration, every acid of the homologous series reduces the surface tension by almost twice the amount of the preceding one. This could be shown to hold up to undecylic acid.[9] The same behavior is exhibited by solutions of alcohols, esters, amines, urethane, etc. If we apply the Gibbs' Adsorption Law, it follows that the amount of the adsorbed substance in the surface increases in the same regular manner.

Langmuir[10] has shown that this rule has the following significance: The work which is required to bring a molecule of the organic substance from within the liquid to the surface, when dealing with low concentrations, increases by a constant amount as we pass from one substance to that which stands above it in the homologous series. The fact becomes thus evident that their attraction by water decreases with increasing molecular weight, and that each CH_2 group manifests its influence to the same degree; we must therefore assume that their carbon chains lie flat in the surface.

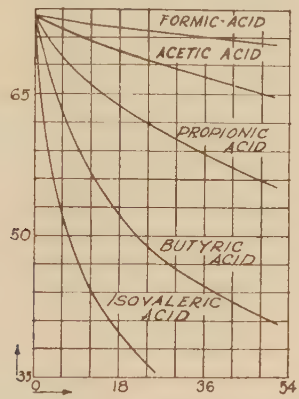


FIG. 3.

The same rule is met in the adsorption of organic substances from aqueous solution with adsorbents like carbon, etc. The depression of the surface tension cannot be measured in such cases, but the adsorption can be directly determined. The adsorption isotherms of several fatty acids in water, using carbon, are shown in Fig. 4, and it is obvious how with a given concentration, the adsorbed amount for the homologous series increases very markedly, being approximately one and a half times as great as we pass from one acid to the next higher one. This has also been found to be the case with the urethanes. Langmuir's explanation need not be changed, and we may assume that the general validity of Traube's Law to be strong evidence that the adsorption in these cases is to be regarded as interfacial concentration.

Perhaps it should be mentioned that the three chloracetic acids decrease the surface tension of the water towards air in a series, which corresponds to that shown by their adsorption by carbon and hide powder.[11] Their adsorption by adsorbents surely has no salt-like character, otherwise we would see a marked increase in adsorption upon changing from monochlor- to trichloracetic acid. Besides surface tension depends upon concentration in such a way, that we can arrive at a relation similar to that of the adsorption isotherm, if we substitute the empirically found values of $\frac{d\sigma}{dc}$ in equation 3a.

However it is unsatisfactory to be content with such qualitative results, and therefore the problem has been attacked from a different angle; adsorption has been considered from the molecular kinetic point of view, *i.e.*, as an attraction of the adsorbent for the molecules of the adsorbed substance. Haber[12] and Langmuir[13] have shown that such an attraction can be expected from the structure of solids. The X-ray spectrometric analysis of crystalline substances has shown that in a crystal of a heteropolar material, like common salt, the atoms, or ions, which make up the substance, form the points of a space-lattice, and the forces which are required to hold the crystal together are the same as those which we regard as chemical forces. For instance, with an NaCl crystal, we have to assume that the Na.˙ and Cl′ ions are alternately at the corners of a cube. Whereas *in the interior* of the crystal the forces of attraction in a lattice plane of atoms are satisfied by the neighboring atoms, this is not the case *at the surface* of the crystal. The attraction of an atom lying at the surface is satisfied toward the interior, but as its force of attraction is also partly towards the exterior, this portion remains unsaturated. These unsaturated attraction forces are supposed to be responsible for adsorption; it is quite probable that this saturation is accomplished not only by specific atoms and molecules, but that all possible atoms and molecules in the gaseous phase or in a solution are involved in it.

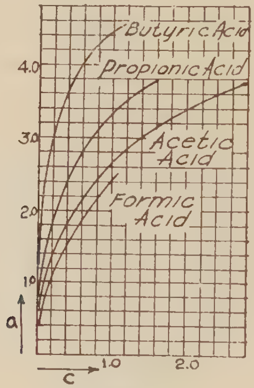


FIG. 4.

In the application of this theory the difficult question arises whether the adsorbed molecular layer consists of one layer of molecules or of *several* layers. Langmuir[3, 13] has developed the view that we are dealing with a monomolecular layer, which need not necessarily be continuous, for there may exist preferential points, the points of residual valence, and only these may be occupied by the adsorbed molecules; thus if the surface be considered as a checker board, only part of the squares are occupied. In contrast to the above, Polanyi has developed a theory in which he assumes a polymolecular or at least a coherent layer. It has not yet been possible to make experiments which would decide in favor of one or the other view; in fact it seems doubtful to me whether it is at all correct to assume, that necessarily only one or the other view is applicable. It seems entirely possible to me, that with substances which are not too strongly adsorbed at low pressure or low concentration, the Langmuir assumption is correct, with more strongly adsorbed materials and higher pressure and concentration, Polanyi's view expresses the facts.

For instance, in the adsorption of methane and other gases by mica plates,[3] of toluol vapors by glass,[4] of the dyestuff Ponceau Red 2R in aqueous solution by $PbSO_4$[15] we are dealing with a monomolecular layer. On the other hand M. H. Evans and H. J. George[16] found that when CO_2 is adsorbed by glass threads at a pressure of about 12 cm. mercury, there are formed adsorption layers 5 to 6 molecules deep (2.5 to 3 $\mu\mu$ in thickness). Euler and his coworkers found a depth of several molecules in the case of the adsorption of silver salts by silver and gold powder.[17] Furthermore Polanyi and his coworkers[14, 18] have calculated the adsorption of several gases and vapors by numerous adsorbents at medium and high pressures, such as the adsorption of CO_2 by coconut charcoal, of SO_2 by silicic acid gel, of benzol, ether, acetone and similar vapors by activated charcoal, and found them to be in agreement with the Polanyi theory, which assumes a polymolecular or at least a coherent layer.

It would lead us too far afield if we were to go into the mathematical discussions of the Langmuir and Polanyi theories. The following should be noted. Langmuir calculates, on the basis of the kinetic theory of gases, the number of molecules which strike against an adsorbent, and the number that adhere to the points of residual valence. His formula leads above all to a "saturation," a maximum of adsorbed substance, as soon as all the points of residual valence have become occupied. This question of saturation may be considered a little more in detail. It should be noted that on the basis of his views, Langmuir is led to assume a quite regular placement of the molecules in the surface. It has already been mentioned above that he concludes from Traube's Law that with large dilutions organic molecules have their carbon chains lying flat in the surface. In the condition of saturation, however, it appears that the carbon chains are extended normally with respect to the surface; but this is only the case with the so-called polar molecules, *i.e.*, those which have groups which differ in their relationship to water. Thus fatty acid molecules turn the hydrophile $COOH$— group which is related to water towards the water, while the hydrophobe CH_3— group, only slightly related to water, is turned outwards toward the gaseous phase.

Polanyi uses the concept *adsorption affinity, i.e.*, the change of the free energy by adsorption, and comes to the conclusion that, in the case of gaseous adsorption, it is independent of the temperature over a wide range; that is, that the adsorption affinity is equivalent to the heat of adsorption. Taking the adsorption isotherm for any *one given temperature*, he is able to arrive at the relation which exists between the adsorption affinity and the quantity adsorbed. Regarding this relation as being generally applicable, he can calculate the adsorption isotherms for other temperatures, and, as has been mentioned above, with good success.

Let us now consider several peculiarities and characteristic cases of adsorption. In the case of gas adsorption, the more easily the gas can be compressed the easier it can be adsorbed. This can also be deduced from Polanyi's theory. We can further conclude that the order in which different gases can be adsorbed by different adsorbents, as charcoal, meerschaum and others, often depends but little on the nature of the adsorbent. The adsorption of hydrogen is apparently much greater than its compressibility indicates. This, according to an observation made by Polanyi, Z. f. Elektroch. **26**, 372, 1920, is a more correct conception than that the rare gases are less adsorbed than their compressibility would lead one to expect. (Freundlich, Kapillarchemie, 2nd Ed., p. 163.)

Upon the basis of the 2nd Law of Thermodynamics, we can deduce from the temperature coefficient of adsorption a relation to the heat of adsorption which is verified by experience. If more than one gas is adsorbed, they will displace each other, *i.e.*, each of the two gases in a mixture will be less adsorbed than if either had been present alone, and the one more strongly adsorbed and having a higher pressure, will displace the one which is not so readily adsorbed and has the lower pressure.

Equilibrium is also easily reached with gaseous mixtures; this is especially true when a strongly adsorbed gas is present in excess over a weakly adsorbed one. During the war such a case arose; it was necessary to remove the small quantities of poisonous gases from the air by means of charcoal contained in air filters. Why carbon (bone black, charcoal) surpasses so extraordinarily all other adsorbents in adsorptivity must still be regarded as an open question. Some are of the opinion that the carbon itself is so active, and that in the preparation of an activated carbon, it is necessary that the extremely fine colloidal state of the raw material (blood, wood) be retained as far as possible, and that substances of high molecular weight which are present in the form of impurities be removed.[19] Others believe, however, that nitrogenous impurities in the carbon are responsible for its adsorptive capacity.[20]

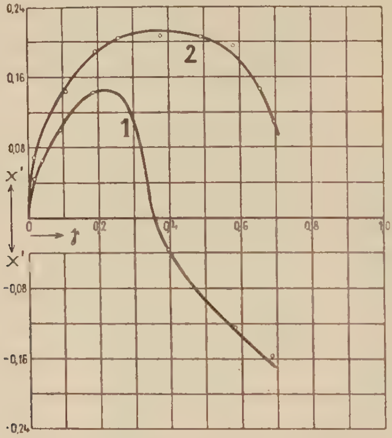


FIG. 5.

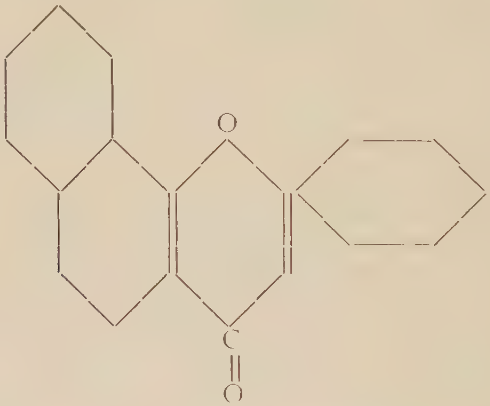
It is a fact that when dealing with adsorption in solutions, there is generally a greater concentration than in the case of adsorption of gases. The changed conditions which exist with higher concentrations become evident, for the views stated previously refer only to dilute solutions and small pressures. We must bear in mind that with higher concentrations not only the dissolved substance is adsorbed but also the solvent, and that with increasing concentration of the solute, the adsorption of the solvent becomes relatively more noticeable. For the same reason we cannot refer the concentration to the volume as is the case with dilute solutions; instead, it is preferable to refer to the weight of substance dissolved in a gram of solution. What is measured is really not the *true* adsorption of the solute, but its *apparent* adsorption; its concentration in the solution after adsorption is indeed greater, because some of the solvent has been adsorbed; thus the adsorbed amount calculated from the difference of the concentrations before and after the adsorption, is too small.

Generally we cannot determine the actual mass adsorbed, because we cannot determine how much solvent has been adsorbed. The adsorption isotherm of the apparent adsorption when investigated up to high concentrations shows a markedly different course than the adsorption isotherm for dilute solutions. Fig. 5 shows two adsorption isotherms. Curve 1 represents the adsorption of acetic acid in toluol by animal charcoal; curve 2 that of phenol in ethyl alcohol by animal charcoal. First of all they reach a maximum which remains constant over a considerable concentration, a condition of saturation to which we have previously referred. With still higher concentrations, the apparently adsorbed percentage decreases, and can actually reach considerable negative values, *i.e.,* the adsorption of the solvent exceeds that of the solute. In order to determine the real from the apparent adsorption, certain experiments have been made whereby the adsorbent is allowed to reach saturation in the vapors of the solution of a volatile substance, such as an aqueous acetic acid solution. Although more work is required in order to reach conclusive results, attention may be drawn to the remarkable regularity of the results which have thus far been obtained.[21]

Let us consider the influence of the nature of the dissolved substance, the solvent and the adsorbent upon adsorption from solutions. Regarding the dissolved substance it has already been noted (cf. above) that Traube's law frequently applies to adsorption as well as to diminution of surface tension. But we must not stretch too far the parallelism between the influence of the dissolved substances upon the surface tension and their adsorption by solid adsorbents. We must not overlook what often happens, that a dissolved substance will not necessarily alter the surface tension in the same manner as it changes the interfacial tension of a solid adsorbent towards a solvent.

Several other conclusions are obtained by the application of Polanyi's theory to adsorption from solutions.[22] It follows that a dissolved substance will in general be more adsorbed the less soluble it is in a solvent. The strong adsorption of difficultly soluble substances is in fact a very common experience; for instance, the strong adsorption of aromatic substances from aqueous solutions in which they are in general only sparingly soluble. Furthermore it follows that if we compare the adsorption of one and the same substance in different solvents which are all about equally well adsorbed, the dissolved substance will be most strongly adsorbed from those solvents in which it is the least soluble. This relation has been well verified for the adsorption of iodine by blood charcoal, in CS_2, $CHCl_3$ and CCl_4.[23] On the other hand if we compare different strongly adsorbed solvents having about the same solvent power for the dissolved substance, then the following rule holds,—in solvents which are more strongly adsorbed, the dissolved substance is less adsorbed. This can in fact be deduced from observations on interfacial tension as influenced by the concentration. A consequence of this rule is that from water, which even with adsorbents like carbon, etc., is not strongly adsorbed, many dissolved substances are very strongly adsorbed; but this is not so in the case of the more strongly adsorbed organic solvents.

If we compare different adsorbents, we often find the regularity mentioned under gas adsorption, namely, that the order in which the different substances are adsorbed is quite independent of the nature of the adsorbent; perhaps the Traube law may even hold for the various adsorbents. Numerous deviations from this rule occur, which are to be expected if adsorption depends upon the saturation of the residual valencies as explained above. We should always bear in mind the possibility that the specific peculiarities of the valency forces of the adsorbent may play a rôle. As an example of such a specific behavior we can take the adsorption of iodine with the accompanying formation of a blue color by different solid substances, although the view that this is an adsorption is not generally accepted. It is known that starch is not the only substance which becomes colored blue with iodine; Barger [24] was able to show that a whole group of organic substances which belong to the xanthone and flavone series are capable of doing so. According to his experiments a definite constitution is required in order that this iodine adsorption take place; the substances must have crossed conjugated double bonds, possibly a structure as found in α-naphthoflavone



If a double bond is destroyed by reduction, the ability to adsorb iodine with blue color formation disappears. The introduction of different groups changes the power of adsorption of these adsorbents, aryl groups for instance causing an increase; this is of interest if we consider that, on the contrary, they increase the adsorptivity of dissolved substances.

Adsorption from mixtures of several dissolved substances requires keen and thorough analysis.[25] The first attempts in this direction indicate that, as in the case of gases, it is simply a reciprocal displacement, the adsorption being preferential for the more strongly adsorbable and the more highly concentrated substance. But new experiments [26] show that under certain circumstances one substance can favor the adsorption of a second, a phenomenon which is still difficult to explain.

A very important but as yet unexplained and difficultly understood group of phenomena is the adsorption of electrolytes. The difficulty arises particularly from the fact that we know even less than is usually the case in adsorption phenomena, whether what we call an adsorption of electrolytes is really one single phenomenon, or whether at present several different phenomena are not included under this head.

A marked limiting case can be observed in the adsorption of the radioactive elements by difficultly soluble salts, or what may be more correctly termed *heteropolar adsorbents*, as for instance $BaSO_4$, AgCl, etc. The rule expressed by Panéth [27] holds here, namely, that a radio active element is generally adsorbed by a heteropolar adsorbent, if the latter is present in higher concentration, and is able to form a difficultly soluble compound of the nature of the adsorbent. Ra is adsorbed by $BaSO_4$ and $BaCrO_4$ because $RaSO_4$ and $RaCrO_4$ are difficultly soluble, but not by AgCl and Cr_2O_3 because $RaCl_2$ RaO are easily soluble. Panéth explains this lucidly as follows: If we regard the solubility equilibria kinetically, in the case of $BaSO_4$, Ba^{++} and SO''_4 ions will initially go into solution, and then separate out on the solid substance. If a radio-element is in solution, which forms a difficultly soluble sulfate, as for instance Th-B isotopic with Pb, it is extremely probable that the Th-B atoms will adhere to the surface of the SO_4'' ions because $ThBSO_4$ is difficultly soluble, whereas for instance ThC which is an isotope of bismuth, because of the greater solubility of the ThC sulfate, will preferentially remain in solution.

The phenomenon observed by Fajans and Beer [28] rests on a similar adsorption according to Panéth, namely, that radio-elements are carried down by difficultly soluble precipitates if their respective compounds give difficultly soluble precipitates. According to unpublished experiments by Hentschel, the Panéth rule appears to hold also for other ions in larger concentrations, as for the adsorption of Pb^{++} by $BaSO_4$, etc. On the other hand capillary active influences are likely to be of greater importance in the case of adsorption by less markedly heteropolar adsorbents, such as the difficultly soluble sulfides, which do not form difficultly soluble sulphides with the adsorbed ions. This adsorption of radio-elements has all through the character of an *exchange adsorption:* For every radio-atom which enters the adsorbent a corresponding atom from the adsorbent enters the solution and it seems plausible to assume that the exchange concerns itself directly with those atoms which are located in the space lattice. These conclusions must be accepted with caution, for according to investigations and observations made by Volmer which will be discussed later (*cf.* p. 586) it seems improbable that under these conditions atoms can enter into the lattice; they must first of all go into an adsorption layer. The similarity with the adsorption of non-electrolytes is thus greater than what had been originally supposed.

We will find many cases of adsorption of electrolytes which indicate such an exchange adsorption, where an ion *of* the dissolved electrolyte is taken up by the adsorbent, while an equally charged ion is given up by the adsorbent to the solution. This is so in the case of the adsorption of many electrolytes, especially actually dissolved dyestuffs, by fibers, kaolin, glass, etc., sometimes also carbon.[29] With carbon it is apparently ash-like impurities which give rise to the ion appearing in the exchange. With substances like fibers, kaolin, glass, etc., the presence of such an ion is obvious. There is every reason to believe that in the great majority of cases it is really such an exchange adsorption and not a *cleavage adsorption,* where perhaps by hydrolysis either H^+ or OH^- ions enter the solution in place of the ion which adheres to the adsorbent. But it would not be wise to exclude cleavage adsorption entirely. Bartell and Miller [30] state that a sugar carbon which has been carefully purified adsorbs methylene blue in large concentration by hydrolysis, whereby H^+ ions take the place of the methylene blue cation. That the usual adsorption isotherm holds in most cases of exchange adsorption must not be accepted as proof that the mechanism is the same as that of the adsorption of non-electrolytes. Thus Panéth [31] has shown that, from the adsorption of ThB by $PbSO_4$, we can calculate the adsorption of the Pb ions, and that from an entirely different hypothesis an equation can be derived which apparently seems to be quite similar to the adsorption isotherm.

Carbon adsorbs most salts not by exchange of ions, or only a small fraction in this way; that is, anions and cations are adsorbed in equivalent amounts.[32] That their adsorption is noticeably independent of each other becomes evident in many ways. Ions of the same sign displace one another, which is also often the case in the adsorption of non-electrolytes. Ions of opposite sign influence each other's adsorption in this sense, that a more strongly adsorbed ion will drag the more weakly adsorbed ion with it onto the surface; thus a weakly adsorbed ion, as for instance the Cl^- ion, will be very slightly adsorbed when in the presence of the weakly adsorbed Na^+ ion, but much more so when in the presence of the more powerfully adsorbed Al^{+++} ions. Rona and Michaelis [33] have shown that the adsorptivity of H^+ and OH^- ions can be separately determined if they are measured in the presence of an excess of other electrolytes, such as KCl, and the like.

It is also noteworthy that Panéth,[31] by means of the adsorption of radio-elements, was able to determine relatively the magnitude of the interface of adsorbents, a task which generally is difficult to accomplish. He succeeded at first only with adsorbents consisting of difficultly soluble salts of an isotopic element. From the very nature of isotopy, in the case, for instance, of the adsorption of ThB by $PbSO_4$, the ratio of ThB to Pb atoms in the solution must be the same as their ratio in the surface. Since we can determine the concentration of the ThB in the solution and of the adsorbed mass in the surface, and furthermore, since we know the concentration of the Pb ions in solution, we get from this relation the number of Pb atoms in the surface and therefore a measure of its size.

II. The Significance of Adsorption for Crystallization Processes

From prior investigations of Marc,[34] but particularly from the more recent work of Volmer,[35] we have come to realize that adsorption plays an important part in crystallization. Although in this respect the last word may not have been spoken, the results obtained so far seem so remarkable and the prospects which they offer so interesting, that I shall consider them more at length.

R. Marcelin [36] had already observed that when *p*-toluidin crystallizes from a supersaturated alcoholic solution, the crystals will always grow in thin layers, as if the newly crystallized substance were, so to say, floated on. Volmer was able to verify this in many other cases. If, for instance, he allowed mercury crystals to grow in supersaturated mercury vapor and followed the crystallization under strong magnification, he saw how rapidly growing layers formed on the mercury surface, began at one place and then spread with constant thickness over the whole surface. PbI_2 behaved similarly when it crystallized from aqueous solution. From this behavior Volmer concluded that crystallization does not proceed by atoms entering the space lattice directly; * they are at first held fast in an adsorption layer, that is, each crystal is able to adsorb on its surface the ions, or atoms of which its space lattice is built. Marc had already come to this conclusion, as he had observed that when fine crystal powder was added to a supersaturated solution of the crystal in question, an initial reduction in the concentration occurred, which was greater than that which takes place later during the course of the crystallization, and which proceeds in a regular manner. Volmer assumes further that the adsorbed atoms, or molecules, are moving freely in the level adsorption layer lying next to the adsorption plane, while it is difficult for them, on account of the force of adsorption, to withdraw vertically from the plane. They behave then like a two dimensional gas; or, if a comparison is permissible, like skaters on a sheet of ice. Furthermore, McBain and Salmon described the peculiar phenomenon which the micells of a soap solution show when they touch a coagulating fiber present in such a solution; they remain attached to it, but are in lively motion along the thread, that is, in a unidimensional Brownian movement. If the moving atoms, or molecules collide unelastically in the adsorption layer, as will be the case if the energy which is given off thereby is taken up by the crystal lattice, a crystal nucleus will be formed in the layer, and this will grow further sideways, whereby the molecules which are in the adsorption space become attached. Volmer's observations are to be thus understood; we can also see that, depending upon the thickness of the nucleus and the adsorption layer, the new expanding crystal layer, which spreads out, may be of varying thickness. From the different interference colors which Volmer found, he had to conclude that there were different thicknesses of layers.

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* See also Chapter I. J. A.

The mathematical proof of these views is hardly possible at the present time, because the amount of adsorption on crystallization planes is not known, and above all because we do not know the different amount of adsorption on the various crystal planes. If we knew more about this, one could, according to Volmer, determine the *velocity of crystallization* of the different planes, which increases in proportion to the strengths of their respective adsorptions. Furthermore, the shape of the crystal depends upon this rate of crystallization. Completely formed crystals have those surfaces in excess which have grown the slowest. Volmer shows, however, on the basis of probable assumptions as to the amount of adsorption at different surfaces, that this may very likely give rise to a ratio of the velocities of crystallization of about 1 : 1000, and such values must be expected, if we want to explain the appearance of leaflets and needle-like crystals.

In good accord with these views stands the influence of impurities upon the velocity of crystallization both with solutions, as Marc [34] had previously shown, as well as with supercooled melts as Freundlich [38] emphasized later. Marc showed that the velocity of crystallization of substances like K_2SO_4, etc., in supersaturated aqueous solutions, is retarded only by such materials as are adsorbed by the crystals—for instance several dyestuffs (quinoline yellow, etc.); the solution of the crystals is not influenced by such substances, which from the standpoint of the theory of diffusion is quite comprehensible. The retardation of crystallization by certain dyestuff concentrations may be so powerful, that it is completely inhibited, although the solution is still strongly supersaturated with respect to the crystallizing material. In the case of small percentages of impurities, the retardation may be expressed by an equation which corresponds with that for the adsorption isotherm. The same holds for the retardation of the velocity of crystallization of supercooled melts in their relation to impurity concentration, as Freundlich has calculated from measurements of Pickard [39] and others. This relation is quite evident: if in addition to the molecules of the crystallizing material the impurity also is adsorbed on the crystal surface, it enters into competition with the molecules, hinders their getting together to form nuclei, and retards in proportion of its mass present at the interface.

The influence of impurities upon crystallization is a phenomenon of general importance.* As the different crystal surfaces adsorb the impurity differently, the velocity of crystallization will be markedly changed by the adsorption and hence also the shape of the crystals. It is probably known how under certain conditions impurities will strongly affect the course of crystallization; for example it will be recalled that in the presence of methylene blue AgCl forms dendritic crystals instead of the regularly formed ones which precipitate from a pure solution. If more were known of this influence, we could tell quite often from crystals occurring in nature from what kind of solution they were originally separated. The peculiarly finely crystalline character shown by structures like urinary calculi, gall stones, etc., which are found in the organism, depends upon the fact that the adsorbed colloids have retarded the velocity of crystallization.[40] The velvet-like soft appearance of ice cream is caused by the presence of gelatin and similar colloids, which on account of the retardation of the velocity of crystallization allow the formation of only extremely fine crystals.[41] In industrial work the purification of a solution by means of carbon is very important, because impurities are thus removed which under certain circumstances can affect the crystallization of a substance, even though it be in supersaturated solution.

Moreover Volmer [42] observes that the formation of nuclei may occur not only on the crystal surface of the same substance, but in general they may also form at all kinds of interfaces. First of all because of adsorption, the concentration of the crystallizing substance becomes greater there and hence the conditions that the required number of molecules which should meet in the required time for nucleus formation are more favorable than in the free solution. Furthermore, the work required for the formation of nuclei in the adsorption layer is smaller, because the free energy for the formation of the surface of the nucleus adjoining the adsorbent, will be as a rule less than what would be required to form a surface of the same size in the free solution. The preferred formation of nuclei at interfaces is an important factor in the formation of Liesegang's rings.

III. THE SIGNIFICANCE OF ADSORPTION FOR REACTION VELOCITY

It has been shown that the majority of gas reactions at low or medium temperatures—below 600°—do not take place in the gas space, but at the walls of the vessel. Hence the time of its reaction is greatly influenced by adsorption phenomena. We also know a whole series of similar adsorption reactions which take place in solution where they may proceed in the presence of an adsorbent like carbon, or in a colloidal solution. Study of a whole series of important biological reactions indicates that they unquestionably take place at interfaces.

It has frequently been assumed, when a gas reaction is strongly accelerated at the wall of a vessel, that this is sufficiently explained by the fact that because of increased concentration in the adsorption layer, the adsorbed substance decomposes more rapidly or reacts with the adsorbent more rapidly because of an intermediate reaction. But according to Polanyi [46] this influence alone is not enough in order to explain the large increase in the reaction velocity. He estimates, for instance, that Bodenstein's experiments on the catalysis of oxyhydrogen gas at porcelain walls at 600° should hasten the reaction 10^8 times as compared with the gaseous space; from the probable adsorption of H_2 and O_2 we can calculate a condensation of 5 to 10 times and from it an acceleration of $10^{2.5}$. Hence Polanyi suggests a different cause for this extraordinary increase. From certain theoretical reasons, which can only be mentioned here, he believes that atoms must have a considerably greater heat of adsorption than molecules. The adsorption space must therefore be regarded as a zone of increased dissociation, for the negative heat of dissociation of molecules like H_2, O_2, etc., otherwise so great, is smaller in the adsorption zone because the greater heat of adsorption of the atoms produces an increase in heat there. It is this increased dissociation which is primarily responsible for speeding up the reaction.

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* In household and commercial practise, use had long been made of inhibitors of crystallization—*e.g.*, gelatin in ice-cream, gum arabic in confectionery, etc. One of the earliest publications on this subject is "The Effect of Colloids on Crystalline Form and Cohesion," by Wm. C. Ord, M.D., a book published in London in 1879 (see *Science*, 1925), which contains a wealth of interesting data. J. Alexander (*Koll. Zeit.*, 4, 86, 1909) treated this question; and R. E. Liesegang (*Koll. Zeit.*, 5, 96, 1910) treated the converse question—the forms produced in jellies by crystals forming in these. J. A.

As a rule the conditions of these adsorption reactions are not altogether so simple; either the initial substances or the reaction products may be preferentially adsorbed. They may mutually displace each other, the adsorption layer may hinder the entrance of one of the reacting substances to the interface, etc. Each case has its peculiar characteristic and one must be careful in drawing conclusions from one reaction for application to a similar one.

The conditions are simple when the reaction products are adsorbed only slightly or not at all, while one of the initial substances is powerfully adsorbed. In such a case the reaction velocity is generally proportional to the adsorbed mass of the initial substance, and this can be connected up with the concentration in the gaseous space, or in the solution, on the basis of the adsorption isotherm. A good example of this sort is the decomposition of antimony hydride into hydrogen and antimony at ordinary temperature, according to the equation.

$$4SbH_3 = 4Sb + 6H_2$$

with Sb as adsorbent.[45] The Sb formed by the reaction produces an increase in the adsorbing surface. But if we make the amount of Sb initially present, large enough, by letting the reaction take place, let us say, in a vessel covered with an antimony mirror, we can then disregard this increase and hence assume that the adsorbing wall surface is of constant size. The adsorption of hydrogen can be considered to be slight and therefore we have to consider only the adsorption of SbH_3. Hence we can assume that the decrease in pressure $-\frac{dp}{dt}$ is simply proportional to the adsorbed mass, x. Applying the adsorption isotherm, $x = \alpha \,.\, p^{\frac{1}{n}}$, and combining all of the constants into one constant, k, we get the reaction equation $-\frac{dp}{dt} = kp^{\frac{1}{n}}$, which when integrated is

$$k = \frac{1}{\left(1 - \frac{1}{n}\right)(t_2 - t_1)} \left[p_1^{-\left(1 - \frac{1}{n}\right)} - p_2^{\left(1 - \frac{1}{n}\right)}\right] \qquad (4)$$

This equation was confirmed by observation. In accordance with the theory of adsorption, the value of $1/n$ increases with increase in temperature. Similar gas reactions are the decomposition of P and As hydrides, as well as that of selenium hydride on selenium surfaces.

The equation (4) holds also for a series of cases dealing with adsorption in solution, as for instance the decomposition of formic acid on rhodium according to the equation,

$$H.COOH = H_2 + CO_2$$

and by the reaction between Na hypophosphite and H_2O on Pd black, according to the equation,

$$NaH_2PO_2 + H_2O = NaH_2PO_3 + H_2$$

and particularly by the decomposition of H_2O_2 in a Pt sol

$$2H_2O_2 = 2H_2O + O_2.$$

For the decomposition of formic acid and hydrogen peroxide we have every reason to assume that the reaction products are weakly adsorbed and hence do not disturb the course of the reaction at the surface.

If there is more than one initial substance, say two, both of which are markedly adsorbed, one circumstance must be considered to which Reichinstein[46] has already called attention. The substances will mutually displace each other from the surface, especially if one or the other is present in greater concentration, while with a medium concentration a maximum velocity reaction will be found. Reichinstein explains amongst others, the remarkable cases where, for instance, oxygen is used in oxidation processes, with medium O_2 pressures, a maximum reaction velocity sets in; examples of this kind are the glowing of P by its oxidation in air, the oxidation of aldehyde, of silicon hydride by oxygen, etc. Reichinstein also tried to express these relations numerically, by assuming that the number of molecules present in the adsorption layer remains constant with all adsorbed substances and with all pressures, an assumption which, however, can hold only approximately.

If the end products are mainly adsorbed, we generally have a reaction of materially different character. When compared with the reaction in the gaseous space or in pure solution, there is naturally an acceleration of the reaction of the adsorbent because the initial products which are also adsorbed react more quickly at the surface; but the adsorption layer, formed mainly from the end products, will finally have a retarding effect, because it opposes the diffusion of the initial products to the boundary surface, or because the end product displaces the initial substances. Several cases are known which can be satisfactorily explained on the assumption that the velocity of reaction is determined by the velocity of diffusion of one of the reacting substances through the adsorption layer. Bodenstein and Fink[47] have investigated the kinetics of the gas reaction $2SO_2 + O_2 = 2SO_3$ on a Pt surface. SO_3 is adsorbed most powerfully and is the main constituent of the adsorption layer. As the velocity of a reaction always depends upon the rate of the slowest process, it depends upon the inward diffusion of that initial substance which is present in lowest concentration; the one in largest concentration is of course present in sufficient amount at the surface. Considering the laws of diffusion solely, and assuming that the thickness of the adsorption layer is proportional to the amount of SO_2 adsorbed, we get the equation

$$\frac{d(2SO_3)}{dt} = k_y \frac{(2SO_2)}{(2SO_3)^{1/n}}$$

for the case when oxygen is present in excess. The parenthetical expressions represent concentrations. If on the other hand SO_3 is present in excess, the corresponding equation would hold

$$\frac{d(2SO_3)}{dt} = k_z \frac{(O_2)}{(2SO_3)^{1/n}}.$$

The constants k_y and k_z depend in characteristic fashion upon the diffusing substances SO_2 and O_2. This view has been completely confirmed by experiment.

According to Bodenstein and Fink [47] the catalysis of oxyhydrogen (under certain conditions) belongs to this group of gas reactions, also the splitting of CO_2 into CO and O on Ni and Co surfaces, etc. According to Freundlich and Bjierke the reactions in solution of the oxidation of phenylthiourea by oxygen on carbon surfaces, takes place similarly; it depends upon a diffusion of oxygen through an adsorption layer which is essentially built up of the reaction products.

There are indeed cases where an initial substance, because of its strong adsorption, delays the diffusion of a second reacting substance, so that it hinders its own reaction. This is particularly the case in the oxidation of oxalic acid by oxygen in aqueous solution on carbon surfaces.[49] The kinetics of the process can be calculated by assuming that O_2 is forced to diffuse through an adsorption layer of oxalic acid.

It is perhaps more probable in other reactions that a retardation is due to the presence of other substances, especially of impurities added purposely, which displace one of the adsorbed substances at the interface. This holds particularly for the action of many capillary-active substances like urethane, etc., when they retard the oxidation of amino acids by carbon. O. Warburg and Negelein [56] found that this retardation is just as great, if the adsorbed amount of the various capillary active substances is equivalent. The agreement became even better if the retardation was calculated in cases where the surfaces covered with adsorbed molecules were of equal size. Traube's Law (compare p. 578) naturally comes very much into evidence. The same retardation is reached, when ascending the homologous series of urethanes; the concentration for the next higher urethane is about half what it is for the preceding one.

O. Warburg [51] uses the validity of the Traube's law in order to decide whether or not a biological reaction takes place at interfaces. No case is known where this law holds for a reaction in homogeneous solution; for instance it does hold for the inversion of sugar by invertase, but it does not hold when the inversion is accomplished by acids.[52] Fermentation, respiration and CO_2 assimilation have been found to be retarded by urethanes according to Traube's law, and Warburg deduces from this that all these processes take place at interfaces.

The investigations of Warburg have further shown that with all these reactions, a finer mechanism must be taken into account. The influence of capillary-active substances, as already mentioned, can be satisfactorily referred to their adsorptivity. But there are substances, as for instance, hydrocyanic acid, which are more powerful retardants than the latter, although much less adsorbed. O. Warburg [53] was able to show that the Fe content of the blood charcoal used for the experiments is crucial for this behavior. An iron-free sugar char likewise accelerated the oxidation of amino acids, but this process was not checked by hydrocyanic acid. We must therefore assume that while oxidation takes place partly on the charcoal, still, certain iron-containing interfaces are particularly active, and the reason why the HCN retards so powerfully is because it forms an unstable compound with the iron, probably analogous in form to an adsorption compound. The influence of capillary-active materials is just as comprehensible as ever; on adsorption they cover the iron-containing as well as the iron-free spots in the interface. Observations made by Elissafoff[54] show very distinctly how strong the catalytic action of adsorbed metals on interfaces can be. The decomposition of H_2O_2 in aqueous solution is strongly accelerated by glass wool as well as by dilute Cu salt solutions; glass wool and Cu salts act together very much more powerfully than either of these substances alone, and it can be shown that the action is proportional to the amount of Cu adsorbed on the glass wool.

The possibilities which must be considered regarding the micro-structure of adsorption layers are not yet exhausted. The characteristics mentioned (p. 580), as to the position of polar molecules in the interface, is most probably also important for adsorption reactions. Recently Kruyt and van Duin[55] have explained from this point of view why certain reactions, as for instance, the reciprocal action of the Na salt of p-sulfodibromhydrocinnamic acid with KI in the presence of carbon is stopped, while the corresponding reaction between dibromsuccinic acid and carbon is accelerated: In the first case we can assume that both of the Br groups are diverted from the aqueous phase and therefore react less easily with the I ions. In the second case we have reason to believe that the two Br groups are turned towards the aqueous phase.

Probably we will be able to include enzyme reactions, on the basis of their kinetics, in the class of adsorption reactions; as we know relatively little in that direction, this hint must suffice.[56]

Thus much for reactions which take place at interfaces. Not less important are the cases when a chemical equilibrium is diverted at an interface. We can predict theoretically on the basis of the second Law of the Thermodynamics: Equilibrium is shifted in the sense that the formation of capillary-active substances at the interface is favored, the formation of capillary-inactive substances being opposed. Such phenomena have not yet been closely investigated.[56, 57]

IV. The Significance of Adsorption for Colloid Formation

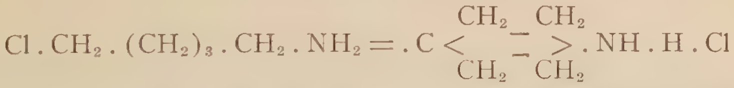
It is not possible within the scope of this article to discuss the many cases where adsorption is certainly or probably of importance for colloidal structures. In the previous section several cases have already been pointed out, namely, the function of adsorption in the kinetics of colloidal solution, for instance, in the decomposition of H_2O_2 by colloidal Pt hydrosol or in enzyme reactions. In the following first of all we shall discuss the importance of adsorption for the stability of colloidal solutions. It is true that here we tread upon rather uncertain ground; for the adsorption involved is an adsorption of electrolytes which closely resembles an exchange adsorption. Opinions differ as to whether we have any right to class it amongst adsorption phenomena, and also as to the nature of its characteristics.

The colloidal solutions whose stability shall be considered are the so-called hydrophobic sols, which are relatively unstable and are precipitated by low concentration of electrolytes; for instance, to this group belong the unprotected sols of the metals (of gold, silver, etc.), of sulfides, many hydroxides (Fe and $Al(OH)_3$, etc.). It is known that to retain their stability there is required a certain small amount of an electrolyte. This becomes evident from experiments by Lottermoser[59] with AgI sols. If a dilute solution of $AgNO_3$ is treated with dilute KI solution or vice versa, the sol is not stable, if exactly equivalent amounts are measured; but it is stable, if a small excess of either one or the other substance is present. The sol is positive if Ag^+ ions are in excess, negative if I^- ions are in excess. The ion which is present in excess appears generally to be fixed according to an adsorption isotherm. This is true, for instance, according to experiments by Maffia,[60] for the binding of Cl^- ions in Fe_2O_3 sols.

The attempt has recently been made to conceive this sort of fixation of electrolytes on colloidal particles as a combination similar to complex salt formation, *i.e.*, to assume valency action, as with the Werner salts. Although I think it entirely possible that a gradual transition may be traced between a Werner bond and an adsorption linkage, still I must emphasize, that with our present knowledge, we cannot distinguish the Werner's salts in their reactions from organic substances, whereas their resemblance in behavior to adsorption compounds is very slight. For instance, the change of purpurochrome salts or cobalt salts into their corresponding roseo salts, according to the equation

$$[Cr(NH_3)_5Cl]Cl_2 + H_2O = [Cr(NH_3)_5H_2O]Cl_3$$

agrees exactly with that of ε-chloramylamine to piperidine chlorhydrate.



$$Cl\,.\,CH_2\,.\,(CH_2)_3\,.\,CH_2\,.\,NH_2 = .\,C < \begin{matrix} CH_2 & CH_2 \\ CH_2 & CH_2 \end{matrix} > .\,NH\,.\,H\,.\,Cl$$

Both are slow reactions of the first order, and in addition the dependence on the nature of the halogen is quite analogous; in both cases the halogen is removed from the inner sphere of reaction to the outer.[62] It hardly needs to be shown how different the exchange of halogen is in the particles of an Fe_2O_3 sol.

Colloidal particles will be positively or negatively charged depending upon whether the cation or anion is adsorbed in excess. The character of the charge is generally determined from the direction in which they migrate during cataphoresis. For coagulation the nature of the charge is critical;[63] we always have to consider the nature of the oppositely charged ion, with a positive sol the nature of the anion, with a negative that of the cation. The similarly charged ion is, however, not without effect, but its influence is so much smaller than that of the oppositely charged ion, that it can be neglected for the present. Essentially then the particles are simply discharged by oppositely charged ions, although a complete discharge is not necessary as was formerly believed. That the colloidal particles actually attract preferentially ions of opposite charge, follows very clearly from experiments made by Fajans and v. Beckerath.[64] They showed that silver halide sols (according to Lottermoser) when positively charged by means of an excess of Ag^+ ions, do not markedly adsorb thorium B^+ cations; they do so, however, very strongly when negatively charged with excess halogen ions.

It is not easy to compare the potency of different electrolytes in coagulating a sol. We are dealing in fact with a transitory reaction, and hence we must compare the electrolyte concentrations which produce the same velocity of coagulation. To a certain extent this has been done in only one case, by Gann[65] for the coagulation of Al_2O_3 sol by a large series of electrolytes. But even against these experiments certain objections may be raised, because the method of measuring, the observation of increase in viscosity of the sol, is not above criticism. In other work, the experimenters were satisfied to choose certain concentrations which are comparable because of definite characteristics, either comparing the concentrations which just cause turbidity, or that which in a definite period of time, about two hours, will cause complete flocculation. Very fortunately these values, which will be designated in the following as *coagulation figures,* have a definite meaning from the standpoint of the velocity of coagulation.[66] The latter increases so extraordinarily with small electrolyte concentrations, that the concentration which just causes turbidity is sharply marked as a threshold figure. On the other hand with certain larger concentrations we find with regularity a constant maximum coagulation velocity, the velocity of the so-called instantaneous coagulation;[67] and hence the coagulations become comparable when this velocity is reached.

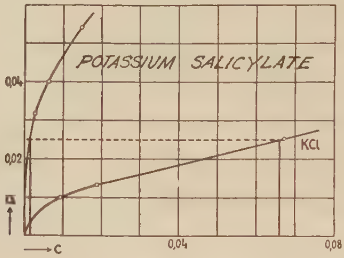


FIG. 6.

As already mentioned, the coagulation figures are in the first place dependent on the nature of the oppositely charged ion, with positive sols on the nature of the anion, with negative sols on that of the cation. They are distinguished by the fact that they move in an exceedingly wide field of concentrations; under the ordinary experimental conditions from several hundred millimols per liter up to a few hundredths of a millimol per liter.[63] This is explained as follows: Experience teaches and theory indicates likewise, that conditions for coagulation prevail, when equivalent amounts of the oppositely charged ion are adsorbed by the colloidal particles. Thus, if we have ions of equal value, which, however, are adsorbed to a different extent, the relation is that shown in Fig. 6, where the salicylate ion represents a strongly adsorbed ion and the Cl ion a weakly adsorbed ion. In order that equivalent amounts should be adsorbed, the equilibrium concentration in the solution must be very different, far smaller for the more powerfully adsorbed ion than for the weakly adsorbed one. In the first case the coagulation figures which are really total concentrations and not equilibrium concentrations, run parallel to the equilibrium concentrations; for the latter this also holds true.

Very striking is the large difference in the coagulation figure with ions of different valence. The more highly charged ions have a much smaller coagulation figure than the lesser charged ions. In order to understand this, we do not need to assume that the more highly charged ions are more strongly adsorbed. We can understand such behavior by merely assuming that the different ions, expressed in moles, are equally well adsorbed and we know, indeed, cases, for instance, in the adsorption of different cations (NH_4^+, UO_2^{++}, Ce^{+++} ion and others) by As_2S_3 powder, where ions of different valence are approximately equally well adsorbed in equimolar solutions. If for the sake of simplicity, we assume that in equimolar solutions they would be equally well adsorbed, then the adsorption isotherm, Fig. 7, would hold for mono, di, and tri valent ions.

Now it must immediately be evident how much the equilibria concentrations must vary, in order that equivalent amounts be adsorbed, which indeed, is necessary for a comparable coagulation. The adsorbed amounts for mono, di, and tri valent ions must be in the proportion 1 : ½ : ⅓. If we substitute once more for the equilibrium concentration the coagulation figure and consider that, as already mentioned (p. 576), the adsorption isotherm when logarithmically plotted gives a straight line, it follows, that we must obtain a straight line when the logarithms of the coagulation values of mono-, di- and tri-valent ions are plotted against the logarithms of 1, ½ and ⅓. To show how far these considerations hold, let me give two examples. In Table I there are given the coagulation figures of a positive Al_2O_3 sol with anions of different adsorbability and different valence.[65] These are reasonably free from objection, as they are concentrations which cause the coagulation to proceed with approximately the same velocity. With these coagulation figures expressed in millimols, are compared the adsorbed amounts expressed in milliequivalents. It will be seen how extraordinarily strongly the coagulation values are differentiated, while the adsorbed amounts vary only very little.

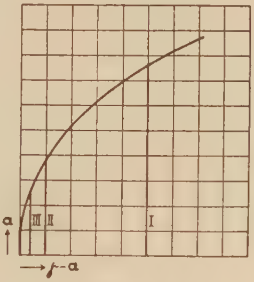


Fig. 7.

TABLE I

Comparative Amounts of Anions Adsorbed by the Flocks, in the Flocculation of Al_2O_3 Sols

Anion	Coagulation Figure (Millimols per Liter)	Quantity Adsorbed at the Coagulation Figure (Milliequivalents per Gram Al_2O_3)
Salicylate	8.00	0.46
Picrate	4.00	0.275
Oxalate	0.36	0.55
Ferricyanide	0.10	0.42
Ferrocyanide	0.08	0.44

In Table II are found the coagulation figures of salts having cations of different valency, determined with respect to a negative As_2S_3 sol. Here we are dealing with complex cobalt salts, where we may perhaps assume, because of their close relationship, that in equimolar solution they are adsorbed to the same extent. If this is assumed and we arrange as in Fig. 8 the logarithms of the coagulation figures as abscissa the logarithms of 1, ½, ⅓, ¼, ⅙, that is, 6, 5, 4, 3, 2, 1.5, and 1, we actually obtain a straight line, and from the theoretical course of this adsorption isotherm, we can calculate the coagulation figures and compare them with the observed values in Table II.

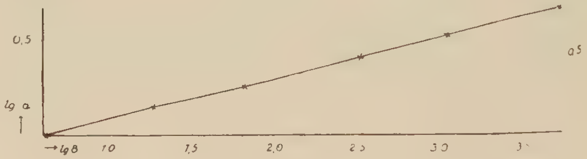


FIG. 8.

TABLE II

COAGULATION OF As_2S_3 SOL BY COMPLEX COBALT SALTS

Electrolyte	Coagulation Figure (Millimols per Liter)	
	Found Experimentally	Calculated
$[CO(NH_3)_4C_2O_4]Cl$	6670	—
$[CO(NH_3)_4NO_2{}^1{}_2]Cl$	5330	—
$\frac{[CO(NH_3)_4CO_2]_2SO_4}{2}$	5330	—
$[CO(NH_3)_4(NO_2)_2{}^1{}_6]Cl$	4670	—
Average	5330	5130
$[CO(NH_3)_5NO_2]Cl_2$	400	—
$[CO(NH_3)_5SCN]Cl_2$	333	—
$[CO(NH_3)_5Cl]Cl$	333	—
Average	333	333
$[CO\,en_3{}^*]Cl_3$	80.0	—
$[CO(NH_3)_6](NO_2)_3$	66.7	—
$[CO(NH_3)_6]Cl_3$	66.7	—
Average	66.7	67
$[(NH_3)_5CO-NH-CO(NH_3)_5]Cl_4$	20.8	—
$[(NH_3)_4CO<{OH \atop OH}>CO(NH_3)_4]Cl_4$	16.7	—
Average	18.8	22
$\left\{CO\left[{OH \atop OH}>CO(NH_3)_4\right]_3\right\}Cl_6$	4.2	4.3

* en = ethylenediamine.

As a matter of fact this relation holds also for the coagulation of agglutinizable bacteria by means of cobalt salts of different valence.[70]

Closely connected with the coagulation of hydrophobe sols by electrolytes, is the influence of electrolytes upon the so-called *electro-kinetic processes, i.e.*, upon electrosmosis, cataphoresis, current potentials, etc.[71] With all of these there is involved a reduction of the so-called electro-kinetic potential, the same potential which is so determinative for cataphoresis and the charge of colloidal particles. Accordingly in observing the influence of electrolytes on the electro-kinetic processes we see a similar rôle played by adsorbability and valency of the oppositely charged ions, and we will find that the identical mechanism exists, as has been shown just now to be operative in coagulation. As the adsorption in this case has not been definitely determined, we will not go further into this phenomenon.

There is a series of other colloid chemical processes in which adsorption is certainly of considerable importance, even though they have not been so lucidly explained. These are the phenomena which appear when hydrophilic colloids like gelatin, albumin and others act upon hydrophobic sols. As is known, there are two possibilities: a small concentration of many of these hydrophilic colloids *sensitizes, i.e.,* in their presence a smaller concentration of the electrolyte suffices to cause coagulation than in their absence. With larger concentrations they act, however, protectively—some colloids appear to exert exclusively a protective action—*i.e.,* coagulation by electrolytes is strongly influenced, it requires a much greater concentration than in the absence of the colloid. When Fe_2O_3 sol was sensitized by albumin it can definitely be shown that an adsorption-like combination between Fe_2O_3 particles and albumin takes place[72] and for the protective action of gelatin for gold, the same condition holds.[73] The peculiarities of these reactions still raise many a problem which is not yet definitely solved and which will therefore not be further discussed here. It may, however, be stated that perhaps a special position of the hydrophilic colloid particles in the adsorption space, similar to that which Langmuir (p. 576) had assumed, might have to be invoked in order to explain the observed phenomena.[74]

Finally just a word about the so-called *retrogression of adsorption.* If a sol be coagulated by means of a dyestuff, it is sometimes observed that initially the solution becomes entirely colorless, because the coagulated flocks have carried all of the dyestuff with them. In the course of time the solution becomes colored however, for the flocks have become larger, more crystalline and on account of the concomitant surface reduction, the adsorbed substance is in large measure returned to the solution. The velocity of the diminution in surface can be followed by means of the velocity of the retrogression in adsorption. Similar phenomena are also met without coagulation taking place, as for instance, in the crystallization of melts containing impurities, or in the precipitation of crystals from solutions containing impurities. The fine crystals which are first precipitated are often at first uniformly surrounded by impurities; they become coarser with lapse of time and force the impurities out, similar to what was observed in the retrogression of adsorption.

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Adsorption by Precipitates

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The contamination of precipitates by adsorption of substances dissolved in the solution from which they separate is a general phenomenon; but the extent of such contamination varies widely with different precipitates, depending as it does on the nature and physical character of the solid and on the nature and concentration of the salts in solution. As a rule the less granular and more finely divided a precipitate, the greater the adsorption; but this is not always the case. Thus barium sulfate thrown down in a crystalline form from a hot dilute hydrochloric acid solution containing potassium chloride, adsorbs potassium quite strongly whereas lead sulfide formed under similar conditions, carries down relatively little potassium in spite of the amorphous character of the precipitates. The tendency of barium sulfate to carry down potassium salts characterizes its behavior toward a large number of other substances. For this reason it will be used to illustrate the phenomenon of adsorption during precipitation.

Because of the intrinsic importance of barium sulfate in quantitative analysis, its adsorptive power has been the subject of numerous investigations. More than 50 years ago Glendenning and Edgar [1] observed that this salt precipitated in the presence of soluble ferric salts carried down iron in some form. Schneider [2] suggested that the iron salt forms a solid solution with the insoluble sulfate; while Richards [3] compared the contamination with ferric sulfate to the occlusion of hydrogen by palladium, a phenomenon which probably involves both solid solution and adsorption. Most investigators are now of the opinion that the carrying down of iron as well as other substances during the precipitation of barium sulfate is primarily an adsorption process.[4] Indeed the adsorption theory seems to offer the only plausible explanation of the fact that this salt carries down all manner of substances from either true [5] or colloidal solutions.[6]

The first systematic investigation of the adsorption by barium sulfate of a large number of cations under strictly comparable conditions was made by Johnston and Adams.[7] The results of their observations as recorded in Table I give the amounts in millimols and milliequivalents of the sulfates of the various metals adsorbed by 1 gram of barium sulfate when precipitated from solutions about 0.003 N in hydrochloric acid and containing the metallic chlorides in the initial concentration $A = 0$ and $B = 0.1$ N. The time of precipitation was 4 minutes and the time of standing 4 hours. The adsorption values obtained under these conditions are of the same order of magnitude; nevertheless they show considerable variation. If the values are expressed in equivalents, one can detect the tendency for ions of higher valence to be more strongly adsorbed in accord with what is known as Schulze's Law.[8] This tendency is less marked if the adsorption values are expressed in mols. Moreover, when so expressed the adsorbability of trivalent aluminum is less than that of either the univalent or divalent ions. In this respect

TABLE I

Metals	Sulfate Adsorbed by 1 Gram Barium Sulfate			
	A		B	
	Milliequivalents	Millimols	Milliequivalents	Millimols
Magnesium	0.048	0.024	——	——
Lithium	0.033	0.033	0.040	0.040
Sodium	0.029	0.029	0.043	0.043
Potassium	0.033	0.033	0.035	0.035
Aluminum	0.051	0.017	0.060	0.020
Ferrous iron	0.074	0.037	0.120	0.060
Nickel	0.062	0.031	0.100	0.050
Copper	0.082	0.041	0.100	0.050
Zinc	0.080	0.040	0.100	0.050
Manganese	0.128	0.064	0.160	0.080
Cadmium	0.160	0.080	0.180	0.090

aluminum appears quite different from trivalent lanthanum which Frion [9] found to be adsorbed by barium sulfate much more strongly than divalent magnesium.

When an alkali sulfate is precipitated with barium chloride in excess, the most usual procedure in sulfate analysis, the determinations are too low since some sulfate is weighed as alkali sulfate calculated as if it were pure barium sulfate. Opposed to this is the adsorption of chloride probably as barium chloride which tends to make the analytical results too high. The latter effect predominates in the precipitation of H_2SO_4 by $BaCl_2$ and of $BaCl_2$ by H_2SO_4.[10] Hulett and Duschak [11] found it possible to obtain exact results in such determinations by estimating the chlorine content of the precipitate and deducting the barium chloride equivalent from the weight of the crude barium sulfate.

Although the adsorption of chloride ion by barium sulfate is appreciable, Mendelejeff,[12] long ago, showed it to be negligible compared to that of nitrate. This was confirmed in the author's laboratory [13] in the course of an investigation of adsorption of various ions by barium sulfate formed on mixing sodium sulfate with a definite excess of the barium salts of the respective ions. The extent of the adsorption was determined by direct analysis of the washed precipitate. In Table II the ions are arranged in the order of adsorption beginning with the most strongly adsorbed ferrocyanide. From a consideration of this order and of the absolute amount of the adsorption in each case, there is little to suggest Schulze's Law. For although a quadrivalent ion

TABLE II

ADSORPTION OF ANIONS BY BARIUM SULFATE

Anion	Adsorption of 100 Mols $BaSO_4$	
	Gram Equivalents	Gram Mols
Ferrocyanide	13.201	3.300
Nitrate	8.482	8.482
Nitrite	7.467	7.467
Chlorate	5.837	5.837
Permanganate	2.847	2.847
Ferrocyanide	2.695	2.695
Chloride	1.760	1.760
Bromide	0.831	0.831
Cyanide	0.310	0.310
Sulfocyanate	0.220	0.220
Iodide	0.056	0.056

appears to be adsorbed most strongly there are four univalent ions more strongly adsorbed than trivalent ferricyanide. Furthermore, contrary to what is implied in Schulze's Law, there is a wide variation in the amounts of univalent ions adsorbed; nitrate being carried down 150 times more strongly than iodide.

Although chemically dissimilar ions of the same valence may show a wide variation in the degree of adsorption thus indicating that adsorption is a specific property of ions, it was observed that nitrate and nitrite ions, which are more nearly related chemically, were carried down to about the same extent. This suggests that the adsorption of ions by a given disperse phase is determined by two factors: the specific adsorbability of the ion and the valence of the ion. By choosing a series of ions of much the same general character, thus minimizing the specific factor, it is possible to emphasize the effect of valence. For example a comparison of the adsorption of various cyanides by barium sulfate, Table III, discloses an unmistakable tendency for ions of higher valence to be adsorbed most strongly.

TABLE III

Anion	Valence	Adsorption Value
Ferrocyanide	4	13.201
Ferricyanide	3	2.695
Sulfocyanate	1	0.220
Cyanide	1	0.310

On account of the adsorption of both positive and negative ions by barium sulfate and the effect of acids and salts on its solubility, the accurate determination of sulfate as barium sulfate can be accomplished only by choosing the conditions so that errors due to adsorption and to solubility compensate each other.

THE PRECIPITATION OF SOLS

Adsorption of Precipitating Ions.

Thirty years ago Linder and Picton found that the cations of electrolytes added to precipitate colloidal arsenious sulfide were carried down in the precipitate. Since the colloidal particles were negatively charged it seems logical to conclude that the adsorption of positive ions neutralizes the charge on the particles thus allowing coalescence and agglomeration. If this be true, one might expect to find equivalent amounts of various ions carried down during the precipitation of constant amounts of sol. This conclusion has been tested by Whitney and Ober,[14] Freundlich [15] and recently by the author with sols of widely varying concentration. From the results of these observations recorded in Table IV, it will be observed that the amount of adsorption of various ions approach equivalence in case the same sol is considered. However, contrary to Freundlich's belief, the adsorption for the same ions varies widely with different sols, just as might be expected when we consider the possible differences in purity, stability, and size of particles that obtain with different preparations. It will be noted that the variation from equivalence in the adsorption of calcium, strontium, and barium ions for each sol used by the author, is less than in the oft-quoted observations of Whitney and Ober; yet it is not permissible to conclude, a priori, that these variations are the result of experimental error. Some observations on ad-

TABLE IV

Metal	Conc. of Colloid As_2S_3	Adsorption Milli-equivalents per G.	Observer
Barium	6.42	0.115	Weiser
Strontium	6.42	0.107	Weiser
Calcium	6.42	0.093	Weiser
Barium	11.80	0.060	Weiser
Strontium	11.80	0.056	Weiser
Calcium	11.80	0.043	Weiser
Barium	21.50	0.072	Weiser
Strontium	21.50	0.069	Weiser
Calcium	21.50	0.073	Weiser
Barium	29.00	0.049	Weiser
Strontium	29.00	0.046	Weiser
Calcium	29.00	0.050	Weiser
Barium	10.00	0.110	Whitney and Ober[16]
Strontium	10.00	0.082	Whitney and Ober
Calcium	10.00	0.100	Whitney and Ober
Anilin	—	0.074	Freundlich[17]
Neufuchsin	—	0.076	Freundlich
Barium	3.33 (approx.)	0.086	Linder and Picton[18]
$UO_2^{\cdot\cdot}$	4.14	0.088	Freundlich[19]
Cerium	4.14	0.069	Freundlich

sorption during the precipitation of colloidal alumina bear on this point. In these experiments 150 c.c. portions of sol containing 1.15 gram Al_2O_3 per liter were precipitated with 50 c.c. of N/50 electrolyte and the adsorption determined by analysis of the supernatant liquid. The results are given in Table V. In addition to the anions listed, experiments with thiosulfate and phosphate were carried out; but the values for these ions are omitted since their accuracy is doubtful, the first because of contamination of the precipitating solution with sulfate; and the second because of the improbability that the precipitating anion is PO_4''' rather than H_2PO_4' or HPO_4''.

Although the maximum variation in adsorption by alumina is quite appreciable, it is really no greater than observed by Freundlich and Gann[20] with colloidal alumina and much less than found by Freundlich and Schucht[21] with colloidal mercuric sulfide. Yet Freundlich offers his data as proof of equivalent adsorption of ions during the precipitation of sols and attributes the variation to the limitations of the experimental method. This explanation cannot account for the variation noted in Table V. While Freundlich is doubtless right in concluding that adsorption of equivalent amounts will effect neutralization, the actual amount of an ion carried down is determined

TABLE V

Anion	Adsorption Milliequivalents per Gram	Precipitation Value Potassium Salts Milliequivalents per Liter
Ferrocyanide	1.280	0.375
Ferricyanide	1.214	0.400
Sulfate	0.997	0.538
Oxalate	1.142	0.700
Chromate	0.870	1.300
Dithionate	0.657	1.625
Dichromate	0.629	1.775

TABLE VI

Oxalate		Chromate	
Concentration of Solution Milliequivalents per Liter	Adsorption Milliequivalents per Gram Fe_2O_3	Concentration of Solution Milliequivalents per Liter	Adsorption Milliequivalents per Gram Fe_2O_3
1.238 *	0.7000	1.413 *	0.7500
1.308	0.7430	1.474	0.7869
1.378	0.7807	1.618	0.8316
1.447	0.8254	1.752	0.8658
1.584	0.9000	1.885	0.8974
1.752	0.9720	2.015	0.9290
1.949	1.0263	2.144	0.9570
2.144	1.0790		

* Precipitation concentration.

(a) by adsorption of the electrically charged particles during neutralization and (b) by adsorption of salt by the electrically neutral particles during the process of agglomeration and settling. The amounts of (a) are equivalent but the amounts of (b) vary with the nature and concentration of the electrolyte. Salt adsorption by the precipitated sol was clearly demonstrated by experiments [22] with the slightly hydrous Pean de St. Gilles ferric oxide sol, using the potassium salts of oxalic and chromic acids as precipitating electrolytes. The results recorded in Table VI show a gradual increase in adsorption of electrolyte with increasing concentration of the latter above the precipitation value. The increased adsorption above the precipitation value was all due to adsorption by the electrically neutral particles; and it is altogether likely that a large part of the electrolyte carried down at the precipitation value was adsorbed during agglomeration. For this reason, Freundlich's conclusion, that equivalent amounts are adsorbed at the precipitation concentration, cannot be generally true since this would mean either that the neutralized particles do not act as an adsorbent or adsorb all ions to the same extent. Moreover the variability of the precipitation concentration will necessarily result in variation in the degree of saturation of the adsorbent by the adsorbed phase. One should expect the adsorption values of various ions to approach equivalence more nearly the less the adsorption capacity of the precipitated particles. This probably accounts for the values being more nearly equivalent with an arsenious sulphide sol than with an aluminum oxide sol having many times the adsorption capacity.

If the variation from equivalence arises from adsorption after neutralization, then it should be possible to arrange the ions in the order of their adsorbability. From the observations recorded in Table V the order of adsorption is as follows: Ferrocyanide > ferricyanide > oxalate > sulfate > chromate > dithionate > dichromate. Considering the precipitation value of the several ions we find the order of precipitating power beginning at the greatest to be: Ferrocyanide > ferricyanide > sulfate > oxalate > chromate > dithionate > dichromate. The order of adsorption determined directly is the same as the order deduced from precipitation data with the exception of oxalate and sulfate which are reversed. These observations lend support to the view that the most readily adsorbed ion precipitates in lowest concentration and vice versa.

With electrolytes having univalent precipitating ions, the precipitation value is usually so high that the change in concentration resulting from adsorption during precipitation is too small to measure with any degree of accuracy. However, the author has determined the relative adsorbability of univalent ions during the precipitation of sols by an indirect method that consists essentially in determining the effect of the presence of univalent precipitating ions on the adsorption of an easily estimated multivalent ion. In a specific case, colloidal arsenious sulfide was precipitated with mixtures of barium chloride and a chloride of a univalent element and the adsorption of barium ion determined with the results recorded in Table VII. From the observations it will be noted that univalent ions cut down the adsorption of barium in the order: lithium > sodium > potassium > hydrogen. Since, under otherwise constant conditions, one should expect the adsorption of a given cation to be cut down by the presence of a second cation in proportion to the adsorbability of the latter, it follows that the order of adsorbability of the univalent ions is: hydrogen > potassium > sodium > lithium. This is exactly the same as the order deduced from the precipitation values of salts assuming that the salt containing the most readily adsorbed cation precipitates in lowest concentration.

TABLE VII

Electrolyte Added to 100 c.c. Sol Total Volume 200 c.c.	Barium Adsorbed Grams	Precipitation Values Milliequivalents per Liter	
N/50 $BaCl_2$ 35 c.c.	0.0078	$BaCl_2$	3.45
N/50 " 30 c.c. N/2 LiCl 30 c.c..........	0.0039	LiCl	131.3
N/50 " 30 c.c. N/2 NaCl 30 c.c..........	0.0031	NaCl	93.7
N/50 " 30 c.c. N/2 KCl 30 c.c..........	0.0026	KCl	83.8
N/50 " 30 c.c. N/2 HCl 30 c.c..........	0.0015	HCl	65.0

The observations recorded above point to a qualitative relationship between the precipitation value of electrolytes and the adsorbability of the precipitating ions in the sense that the electrolyte containing the most readily adsorbed precipitating ion, precipitates in lowest concentration. But even this qualitative relationship fails to hold in many instances since the precipitation value of an electrolyte is influenced by a number of factors other than the adsorbability of the precipitating ion among which may be mentioned the adsorbability of the stabilizing ion of the electrolyte in question, the purity of the sol, the hydrogen ion concentration, etc. Considering only the adsorbability of the precipitating ion the deduction of Dhar, Sen and Ghosh[23] that the most readily adsorbed ion requires the highest concentration to produce precipitation, is both theoretically and experimentally unsound.

Adsorption of the Stabilizing Ion.

It has been recognized for a long time that the precipitation value of an electrolyte for a sol is larger the greater the adsorbability of the stabilizing ion, the ion having the same charge as the sol. Thus, the precipitation value of sodium hydroxide for a negative platinum sol is five times greater than of sodium chloride because of the marked adsorbability of hydroxyl ion. Other typical examples are given in Table VIII. If the adsorption of the

TABLE VIII

Sol	Sign	Precipitation Value Milliequivalents per Liter			
Pt	Negative	Na*Cl	2.5	Na*OH	13.0
$Fe(OH)_3$	Positive	HCl*	400.0	$BaCl_2$*	9.64
As_2S_3	Negative	K*Cl	33.2	K_4*$Fe(CN)_6$	71.2

* Precipitating ion.

stabilizing ion is sufficiently great, it is possible to bring about a complete reversal of the charge on a sol by adding a suitable amount of electrolyte all at once. Thus if an amount of sodium hydroxide slightly in excess of the precipitation value is added to a highly purified chromic oxide sol, no precipitation takes place but the particles change in sign from positive to negative owing to strong adsorption of hydroxyl ion. Among other examples of such charge reversal may be mentioned the action of NaOH or Na_2HPO_4 on a positive ferric oxide sol[24] and of $FeCl_3$ or $Al_2(SO_4)_3$ on a negative mastic sol.[25]

The action of the stabilizing ion varies with the concentration of electrolyte necessary to cause precipitation. This is partly responsible for the absence of direct proportionality between the precipitation value of electrolytes and the concentration of sol. Thus Kruyt and van der Spek[26] found that the precipitation value of potassium chloride decreases with decreasing concentration of colloid while the precipitation value of barium chloride does not change appreciably with the dilution. Similar results were obtained by Burton and Bishop[27] with colloidal arsenious sulfide and mastic.[28] Some investigations[29] were carried out in the author's laboratory using colloidal chromic oxide, Prussian blue, Péan de St. Gilles ferric oxide and arsenious sulfide. The results of a series of experiments on colloidal ferric oxide and arsenious sulfide are given in Table III and shown graphically in Figures 1 and 2. The concentration of the colloid is expressed in per cent, taking the most concentrated as 100 per cent. The curves in the figures were obtained by plotting concentration against ratio of each precipitation value for a given electrolyte to that of the strongest colloid. In the case of ferric oxide sol, the effect of dilution on the precipitation value of electrolytes is clearly not in accord with Burton and Bishop's rules[30] that the precipitating action of univalent ions increases and of trivalent ions decreases with decreasing concentration of sol; while that of divalent ions is almost independent of the concentration of the sol. With colloidal Prussian blue and chromic oxide as well as with colloidal ferric oxide the precipitation value of all electrolytes decreases as the concentration of the colloid diminishes irrespective of the valence of the precipitating ion. With colloidal arsenious sul-

TABLE IX

PRECIPITATION OF FERRIC OXIDE COLLOIDS

Concentration of Colloid	Precipitation Values of $KBrO_3$	 K_2SO_4	 $K_4Fe(CN)_6$
100 per cent (1.7 g. per l.)	40.1	0.68	0.57
50 per cent	34.4	0.41	0.30
25 per cent	28.0	0.25	0.16
12.5 per cent	25.0	0.16	0.08

PRECIPITATION OF ARSENIOUS SULFIDE COLLOIDS

Concentration of Colloid	Precipitation Values of KCl	 $BaCl_2$	 $AlCl_3$
100 per cent (6.24 g. per l.)	68.3	1.940	0.513
75 per cent	68.3	1.877	0.473
50 per cent	70.0	1.800	0.380
25 per cent	76.7	1.733	0.333
10 per cent	80.0	1.633	0.260

fide the precipitation value of potassium ion increases and of aluminum ion decreases as the concentration of the colloid diminishes, in accord with Burton and Bishop's rules. However, from the slope of the curve in Fig. 2 it is obviously incorrect to say that the precipitating action of divalent barium ion is independent of the concentration of the colloid; this is no more true of barium than of potassium ion.

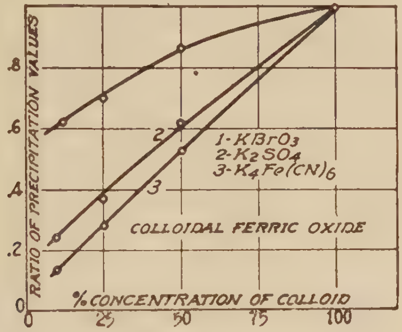

Fig. 1.

Kruyt and van der Spek conclude from their experiments that two factors determine the effect of dilution of a colloid on the precipitation value of electrolytes: First, the decreased number of particles which diminishes the amount of electrolyte necessary to cause sufficient adsorption to lower the charge on the particles to the point where agglomeration takes place; and second, the increased distance between the particles which decreases the chance of collision. This latter effect must be compensated by greater lowering of the charge, hence by the addition of more electrolyte. Since these two factors have opposite effects on the precipitation value, it is only necessary to assume the predominating influence of one or the other in order to account for the results in a given case. Thus, Kruyt and van der Spek assume that the effect which results from changing the chance of collision of particles predominates in the precipitation of colloidal arsenious sulfide with potassium ion; while the effect which follows from changing the amount that must be adsorbed predominates in the precipitation of colloidal hydrous ferric oxide with chloride ion. This difference in behavior with precipitating ions of the

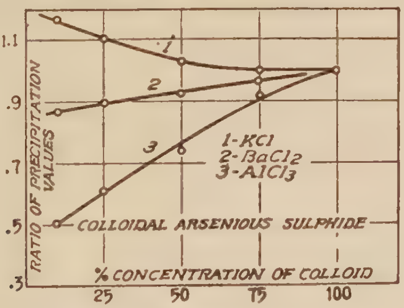

Fig. 2.

same valence is attributed to the hydrophillic properties of hydrous ferric oxide.

Although both of the factors recognized by Kruyt and van der Spek unquestionably have an influence in determining the effect on the precipitation value of changing the concentration of sol, it would seem that these factors in themselves are inadequate to account for all the experimental results. The explanation suggested to account for the difference in behavior of colloidal arsenious sulfide and hydrous ferric oxide with univalent precipitating ions is of doubtful value particularly since mastic emulsion [31] gives results similar to those with colloidal arsenious sulfide although mastic certainly possesses more hydrophile properties than Péan de St. Gilles' ferric oxide. Furthermore, if the decreased chance of collision is the predominating factor that prevents a weaker colloidal arsenious sulfide from coagulating in a given time in the presence of enough potassium chloride to coagulate a stronger sol, it would seem that complete coagulation of the weaker sol should result if sufficient time were allowed. As a matter of fact, however, enough potassium chloride to precipitate in two hours a colloid containing five grams per liter will not precipitate a colloid one-fourth as strong in three weeks. Other observations indicate that Kruyt and van der Spek attach too much importance to the decreased chance of collision of the particles resulting from dilution of sols. Thus, everyone finds that the precipitation concentration varies almost directly with the concentration of sol in case the precipitating ion is of high valence.

That the theory of Kruyt and van der Spek should be inadequate in certain respects might be expected, since these investigators concerned themselves only with the precipitating ions of electrolytes disregarding entirely the effect of adsorption of the stabilizing ions having the same charge as the colloid. If there is no adsorption of the stabilizing ion and if the adsorption of the precipitating ion is very great, there will be a tendency for the precipitation concentration to vary directly with the concentration of the sol. On the other hand, if the stabilizing ion is adsorbed, a greater concentration of precipitating ion will be required to produce coagulation. This effect will be more pronounced the greater the dilution of the sol since the decreased chance both of collision and coalescence will combine to render the sol more stable so that proportionately more of the precipitating ion must be added for complete precipitation. These conclusions are in accord with experimental results.

With electrolytes having multivalent precipitating ions, the influence of the stabilizing ion is frequently very small since the adsorption is so slight at the very low precipitation concentration. Under these conditions the precipitation value decreases to a greater or lesser extent as the concentration of the colloid decreases. As might be expected, the greater the valence of the precipitating ion and hence the lower the precipitation value, the more nearly we find the precipitation concentration varying directly with the concentration of the sol.

With electrolytes having univalent precipitating ions the precipitation value is usually quite large. Although this is generally considered to be due to weak adsorption of the precipitating ion, the adsorption of the stabilizing ion cannot be disregarded at the high concentration necessary for coagulation. In fact, if the adsorption of the two ions is of the same order of magnitude, both may be taken up fairly strongly and a high precipitation value will result. Considerable experimental evidence [32] indicates that potassium ion and lithium ion are fairly strongly adsorbed by arsenious sulfide, the high precipitation value of potassium chloride or lithium chloride for this colloid arising from appreciable adsorption of chloride ion. On the contrary, the high precipitation value of potassium chloride for colloidal hydrous ferric oxide is due to weak adsorption of the precipitating ion, the stabilizing ion having much less effect than with colloidal arsenious sulfide.[33] In general it may be said that the adsorption of the stabilizing ion varies widely but is never negligible if the electrolytes precipitate only in high concentration as is usual with electrolytes having univalent precipitating ions. This adsorption of the ion having the same charge as the sol, renders the latter more stable and proportionately more of the precipitating ion is required for coagulation than in those cases where the influence of the stabilizing ion is negligible. Under these conditions we may expect the precipitation value to fall off much less sharply or even to increase as the colloid concentration is reduced, the increase being greater the greater the valence of the stabilizing ion.

Influence of the Hydrogen Ion Concentration.

Since hydrogen ion and hydroxyl ion are frequently very strongly adsorbed, the stability of sols may be influenced to a marked degree by the hydrogen ion concentration. This is shown clearly by some experiments on the precipitation of colloidal hydrous chromic oxide by electrolytes. Since this sol adsorbs hydrogen ion strongly and so is positively charged as a rule, one should expect the precipitation value of electrolytes to be greater, the higher the hydrogen ion concentration. In the experiments recorded in Table X a chromic oxide sol was precipitated with mixtures of potassium sulfate and sulfuric acid and of potassium oxalate and oxalic acid. The precipitation value of the mixtures and the hydrogen ion concentration, expressed as p_H, before and after precipitation are given in the table. Attention should be called not only to the change in precipitation value but to the shift in order of anions with change in the hydrogen ion concentration. Thus sulfate precipitates in lower concentration than oxalate below a certain p_H value whereas the reverse is true above this value. An investigation of the adsorption of sulfate and oxalate ion through a wide range of hydrogen ion concentration shows the adsorption of oxalate to be greater than that of sulfate throughout

TABLE X

Mixture Added to 5 c.c. of Colloid Total Volume 20 c.c.		Precipitation Value of Anions Milliequivalents per Liter	Ph	
			Before Pptn.	After Pptn.
N/50 $H_2C_2O_4$	N/50 $K_2C_2O_4$			
3.35	0.0	3.35	3.19	3.05
3.15	0.2	3.35	3.32	3.11
2.60	0.5	3.10	3.40	3.17
2.00	0.8	2.80	3.51	3.38
0.00	1.0	1.00	5.79	9.40
N/50 H_2SO_4	N/50 K_2SO_4			
2.50	0.0	2.50	3.12	2.92
2.30	0.2	2.50	3.30	3.00
1.85	0.6	2.45	3.39	3.08
1.25	0.9	2.15	3.74	3.17
0.00	1.1	1.10	5.61	9.35

the entire range, Fig. 3. This result would not be expected if the precipitation value of an electrolyte were determined exclusively by the adsorbability of the precipitating ion.

From a study of the influence of hydrogen ion concentration on the stability of sols toward electrolytes Tartar and his pupils [34] conclude that the precipitation value of all electrolytes for a given colloid is approximately the same at the same hydrogen ion concentration. The author's observations [35] fail to confirm this conclusion. However, as indicated above, two precipitating ions may have the same precipitation value at one very definite hydrogen ion concentration.

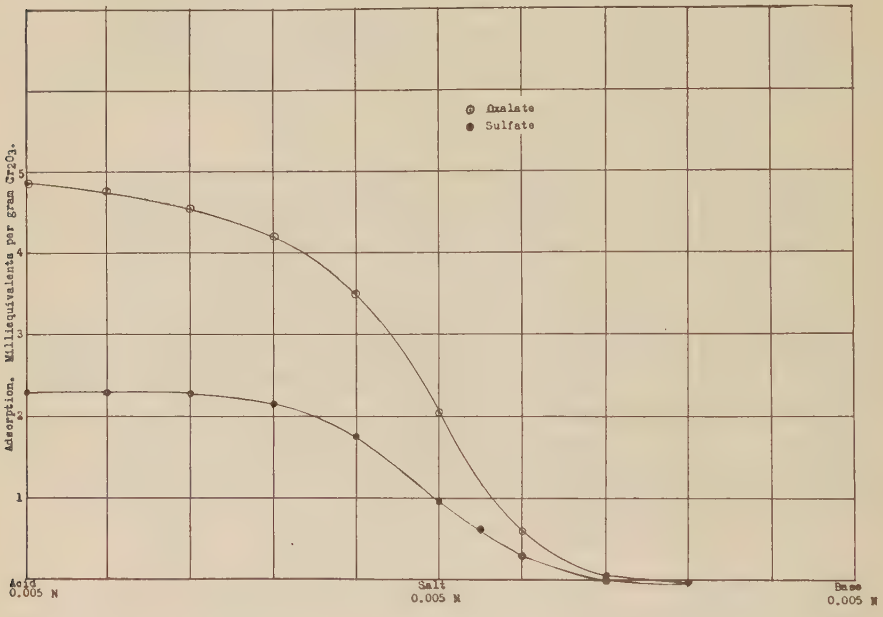

Fig. 3.

Referring to Fig. 3 it will be seen that the adsorption curve is continuous without any evidence of discontinuity such as would be expected if a definite chemical compound were formed at some particular hydrogen ion concentration; moreover, the adsorption varies with different precipitating ions at the same hydrogen ion concentration. Although the adsorption falls off with decreasing hydrogen ion concentration it is appreciable even on the alkali side of the neutral point and is completely nullified only in the presence of an appreciable concentration of hydroxyl ion. Contrary to these observations, Loeb [36] found that only the anions of neutral salts were taken up by gelatin on the acid side of the isoelectric point and only cations on the alkaline side. As a matter of fact Loeb was working at very low salt concentration and so detected no effect of cations other than hydrogen and of anions other than hydroxyl. At higher concentrations of neutral salts the specific effect of ions other than hydroxyl and hydrogen would certainly appear with gelatin as with chromic oxide.

Acclimatization.

For a sol of constant composition the precipitation value is greater when the electrolyte is added dropwise through a long interval of time than when added all at once.[37] This effect is most pronounced with univalent precipitating ions and when there is fractional precipitation of the sol during the dropwise addition. This phenomenon has been termed acclimatization but the term seems to be a misnomer since the sol does not become acclimatized to the presence of electrolyte, in the ordinary sense. The necessity for using more electrolyte for complete precipitation on slow addition arises from the fact that the fractional precipitation continually removes ions owing to adsorption by neutralized particles; and this loss must be compensated for. Moreover, the effect is greatest when the precipitation value of the electrolyte increases with decreasing concentration of sol such as obtains in the precipitation of arsenious sulphide sols with potassium chloride. In this case the fractional precipitation accompanying the dropwise addition of potassium salt produces sols that are successively more and more stable so that a relatively larger amount of electrolyte is necessary for complete precipitation. The factors which determine the excess required for a given slow rate of addition of electrolyte are (1) the extent to which the colloid undergoes fractional precipitation; (2) the adsorbing power of the precipitated colloid and (3) the relative adsorbability of the precipitating and stabilizing ions.[38]

Adsorption from Mixtures of Electrolytes.

In the classic paper to which reference has already been made, Linder and Picton [39] observed that the precipitating action of mixtures of pairs of electrolytes for colloidal arsenious sulfide was not additive in case the electrolytes have widely varying precipitating power.[40] Since this so-called ionic-antagonism was not observed with gold sol and with von Weimarn's [41] sulfur sol which are anhydrous but was observed with Oden's [42] sulfur sol which is hydrous, Freundlich and Scholz [43] conclude that the hydration of the colloid and of the precipitating ions is of primary importance in producing ionic antagonism and so in determining whether the precipitating action of mixtures shall be additive or above the additive values. This leads to the deduction that arsenious sulfide sol is a hydrophile sol although it is not usually so considered; and to the suggestion that the behavior of colloids with mixtures is a suitable means of determining to what extent the stability is influenced by hydration. These conclusions are not in accord with the author's observations [44] with sols of positive hydrous chromic oxide and negative hydrous stannic oxide which possess many of the properties of hydrophile sols. The results of a few experiments with chromic oxide sol are given in Table XI. The figures represent the smallest amount of standard solutions diluted to 10 c.c. that will just precipitate 10 c.c. of sol in 24 hours. Although the sol is very highly hydrous, mixtures of electrolytes having widely different precipitating power such as potassium chloride and potassium sulfate do not give values considerably above the additive value such as Freundlich and Scholz would predict. On the contrary the values for such mixtures are actually *less* than additive by a quite appreciable amount. This might be expected in view of the fact that adsorption is relatively greater at concentrations below its precipitation value so that relatively less sulfate or oxalate is necessary to bring the combined adsorption above the critical value necessary for neutralization and coagulation. Such a result

TABLE XI

Precipitation of Colloidal Cr_2O_3 with Mixtures

(*a*) Potassium Chloride and Potassium Sulfate

N/2 KCl	N/100 K_2SO_4 to Complete Coagulation			
			Difference	
Taken c.c.	Taken c.c.	Calculated c.c.	c.c.	Per Cent
2.27	—	—	—	—
	1.35	—	—	—
0.5	0.85	1.05	−0.20	−19
1.0	0.65	0.75	−0.10	−13
1.5	0.37	0.45	−0.08	−18
2.0	0.13	0.16	−0.03	−18

(*b*) Potassium Chloride and Potassium Oxalate

N/2 KCl	N/100 $K_2C_2O_4$ to Complete Coagulation			
			Difference	
Taken c.c.	Taken c.c.	Calculated c.c.	c.c.	Per Cent
2.27	—	—	—	—
	1.40	—	—	—
0.5	0.92	1.10	−0.18	−16
1.0	0.65	0.79	−0.14	−18
1.5	0.40	0.47	−0.07	−15
2.0	0.14	0.17	−0.03	−18

(*c*) Potassium Sulfate and Potassium Oxalate

N/100 K_2SO_4	N/100 $K_2C_2O_4$ to Complete Coagulation			
			Difference	
Taken c.c.	Taken c.c.	Calculated c.c.	c.c.	Per Cent
1.35	—	—	—	—
	1.40	—	—	—
0.50	0.86	0.88	−0.02	−2
0.675	0.70	0.70	0.0	0
1.00	0.35	0.36	−0.01	−3

TABLE XII

Adsorption by Hydrous Chromic Oxide of Oxalate in the Presence of Chloride

Mixtures Added to 20 c.c. Colloid Containing 0.06 Gms. Cr_2O_3			Oxalate Adsorbed	
N/2 KCl	N/100 $K_2C_2O_4$	H_2O	c.c. N/100	Millieq. per Gram
4.50	1.35	24.15	1.35	0.225
3.00	1.95	25.05	1.95	0.325
1.50	2.85	25.65	2.85	0.475
0.00	4.20 *	25.80	4.20	0.700
0.00	8.50	21.50	7.34	1.223
21.50	8.50	0.00	6.66	1.110
0.00	12.00	18.00	9.42	1.570
18.00	12.00	0.00	8.83	1.472
0.00	15.00	15.00	11.10	1.850
15.00	15.00	0.00	10.68	1.780
0.00	20.00	10.00	12.46	2.076
10.00	20.00	0.00	12.35	2.058

* Precipitation value.

would follow, however, only in case there is little or no antagonistic action between chloride ion and sulfate or oxalate ion in the sense that the presence of each decreases the adsorption of the other at concentrations below the precipitation value. This is evident from the experiments recorded in Table XII.

Below the precipitation concentration, a relatively large amount of chloride has no effect on the adsorption of oxalate; and above this concentration the adsorption of oxalate is cut down but 4 per cent by 50 times its concentration of chloride and less than 1 per cent by 25 times its concentration of chloride. It would appear therefore that the high precipitation value of potassium chloride is due to weak adsorption of chloride ion associated with but slight adsorption of the stabilizing potassium ion. Similar behavior was noted with negative colloidal stannic oxide using mixtures of lithium chloride and either barium chloride or magnesium chloride.

TABLE XIII

Precipitation of Colloidal As_2S_3 by Mixtures of LiCl and $BaCl_2$

N/2 LiCl Taken c.c.	N/100 $BaCl_2$ to Complete Coagulation			
	Taken c.c.	Calculated c.c.	Difference c.c.	Difference Per Cent
4.05	—	—	—	—
	4.03	—	—	—
0.5	4.50	3.54	0.96	27
1.0	4.25	3.03	1.22	38
2.0	3.76	2.03	1.73	84
3.0	2.25	1.03	1.22	118

The action of pairs of electrolytes of widely varying precipitating power on colloidal arsenious sulfide is quite different from the action of such mixtures on chromic oxide. Thus the precipitating action of barium chloride is cut down appreciably by the presence of lithium chloride (Table XIII) so that, in the presence of the latter, the amount of the former must be greatly increased. This is due to the marked effect of the presence of lithium on the adsorption of barium as given in Table XIV. Experiment 1 in this table gives the adsorption of barium ion at the precipitation concentration for barium chloride; experiments 2, 3 and 4 give (a) the adsorption of barium ion from barium chloride alone at the concentration necessary to cause precipitation from the mixture with lithium chloride and (b) the adsorption of barium ion

TABLE XIV

Adsorption by Arsenious Sulfide of Barium in the Presence of Lithium

No.	Mixture Added to 125 c.c. of Colloid Containing 2.84 G. As_2S_3 N/2 LiCl	N/100 $BaCl_2$	H_2O	$BaSO_4$ Remaining in 200 c.c.	Barium Adsorbed Milliequivalents per Gram
I	0.0	50.80	74.20	0.0284	0.072
II	0.0	56.25	68.75	0.0319	0.078
	6.25	56.25	62.50	0.0373	0.056
III	0.0	53.10	71.90	0.0302	0.074
	12.5	53.10	59.40	0.0365	0.050
IV	0.0	47.00 *	73.00	0.0260	0.068
	25.0	47.00 *	48.00	0.0357	0.031

* + 15 c.c. N/100 $MgCl_2$.

in the presence of lithium ion. In experiment 4 the concentration of barium chloride is below the precipitation value, necessitating the addition of some magnesium chloride. Since the precipitating power of these two salts is very nearly the same, the presence of a small amount of magnesium ion can have little or no effect on the adsorption of barium ion at this concentration. The concentration of lithium chloride and barium chloride used in experiments 2, 3 and 4 correspond to those for 0.5, 1 and 2 c.c. of lithium chloride, respectively, in Table XIII.

At the precipitation concentration of a mixture containing one-eighth the precipitation value of lithium chloride alone the adsorption of barium ion is lowered more than 25 per cent; while from a mixture containing one-half the precipitation value of lithium chloride alone, the adsorption of barium ion is decreased 53 per cent. Potassium chloride has a similar effect. On account of the antagonistic action of potassium and lithium ion on the adsorption of barium, the high precipitation value of alkali chlorides cannot be due to very low adsorption of alkali ion which would displace but little barium ion at concentrations below the precipitation value; but is due to fairly marked adsorption of alkali ion associated with appreciable adsorption of the stabilizing chloride ion. Indeed, it is not improbable in the case at hand, that at certain concentrations of lithium chloride or potassium chloride below the precipitation value, the adsorption of chloride ion is actually greater than that of the cation, particularly in the presence of a divalent ion such as barium.[45]

The Influence of Non-electrolytes.

The addition of non-electrolytes to sols frequently results in appreciable sensitization. Thus Billitzer[46] found that a negatively charged platinum sol could be sensitized, discharged, or even changed into a positive sol by the addition of suitable amounts of alcohol; Wo. Ostwald[47] precipitated a silver sol with propyl alcohol; and Klein[48] showed that negatively charged sols of arsenious sulfide, gold, silica, and ferric oxide were agglomerated in part by alcohols, whereas positively charged ferric oxide and silica were not. Freundlich and Rona[49] observed that the addition of camphor, thymol, and urethanes to ferric oxide sol reduced the precipitation concentration of electrolytes.

The sensitization of sols by non-electrolytes has been attributed by Wo. Ostwald[50] and Cassuto[51] to a change in the dielectric constant of the medium. Freundlich[52] suggests that the sensitization results from the lowering of the charge on the particles by adsorption on their surface of the organic non-conductor which has a dielectric constant appreciably lower than that of water. It has been shown that the charge, e, on a single colloidal particle, is

$$e = \frac{EDr(r+d)}{d}$$

where E is the potential difference of the double layer at the surface of a spherical particle of radius r, D is the dielectric constant and d the thickness of the double layer. From this it follows that the lower the dielectric constant the lower the charge on a particle. This would mean that the amount of a precipitating ion that must be adsorbed to effect neutralization will be less and so the precipitation value of an electrolyte will be decreased as Freundlich observed with ferric oxide sol. Furthermore, as the velocity of migration, u, of a colloidal particle in an electric field is given by the expression:

$$u = \frac{EHD}{4\pi\eta}$$

a decrease in D will cause a falling off in u. That such is the case was demonstrated by Freundlich and Rona who found for a pure ferric oxide sol, $u = 0.4 \times 10^{-4}$ cm./sec. for a potential of one volt/cm., while for a sol containing 5 millimols of camphor per liter, $u = 0.2 \times 10^{-4}$ cm./sec. and for one containing 25 millimols thymol per liter $u = 0.3 \times 10^{-4}$ cm./sec. From the slope of the adsorption isotherms, Freundlich also deduced that the decrease in precipitation value will be appreciable only for electrolytes containing univalent precipitating ions that are weakly adsorbed; and will be very slight or negligible for electrolytes containing strongly adsorbed precipitating ions.

From conclusions drawn by Freundlich as a result of his investigations on ferric oxide sol, it would appear to follow that the addition to colloids of non-electrolytes having a lower dielectric constant than water, will always decrease the precipitation value of electrolytes; and that this effect will be greater the lower the dielectric constant of the non-conductor added. These deductions appear to be disproven by the investigations of Kruyt and van Duin[53] on arsenious sulfide sol. The latter found that the effect of non-electrolytes such as phenol and isoamyl alcohol on the precipitation value of electrolytes was determined by the nature of the precipitating ion; for univalent and trivalent ions the precipitation value was lowered; while with bivalent and tetravalent ions it was raised. Moreover, for any given electrolyte the change in the precipitation value seemed to be independent of the dielectric constant of the non-electrolytes employed. Kruyt and van Duin[54] studied the adsorption of non-electrolytes by charcoal and found for a given electrolyte, that there was a parallelism between the effect of different non-electrolytes on the precipitation value for colloidal arsenious sulfide and the adsorption of the non-electrolytes by carbon. However, they were unable to account for the fact that the same non-electrolyte appears to stabilize a sol toward certain electrolytes and to sensitize it toward others. Some experiments of the author[55] throw light on this anomaly: The precipitation value of barium chloride for a sol containing 31.3 g. As_2S_3 per liter was determined both in the presence and in the absence of phenol and isoamyl alcohol. The precipitation values of certain mixtures of $BaCl_2$ and $AlCl_3$ were also determined. The precipitating action of such mixtures is approximately additive.[56] The values expressed in cubic centimeters of solutions necessary to precipitate 100 c.c. of sol in a total volume of 200 c.c. are given under the heading "solutions mixed" in Table XV. The adsorption of barium ion under these several conditions was also determined as given in the last column of the table and as shown graphically in Fig. 4.

Comparing the result of experiment I with that of experiment II, it will be observed that the adsorption is less in the presence of phenol although the amount of electrolyte that must be added to effect precipitation is greater. This means that the sol is sensitized, in the sense that less barium ion must be adsorbed in order to lower the charge on the particles below the critical value necessary for agglomeration and precipitation. The fact that a higher concentration of barium must be present to cause precipitation of the sensitized sol is due to the marked influence of the adsorption of phenol on the adsorption of barium ion. This is demonstrated clearly in experiment III in which the adsorption of barium in the presence of phenol is determined at the concentration of electrolyte that will cause precipitation in the absence

TABLE XV

Adsorption of Barium Ion by Arsenious Sulfide

	Solutions Mixed with 100 c.c. Colloid Containing 31.5 G. As_2S_3				Barium Adsorbed	
No.	N/50 $BaCl_2$ c.c.	Phenol c.c.	H_2O c.c.	$BaSO_4$ Remaining in 180 c.c.	Milliequivalents per Gram	Grams per Mole
I	31.40	0	68.60	0.0502	0.047	0.805
II	42.35	50	7.65	0.0751	0.041	0.708
III	31.40	50	15.00 *	0.0531	0.038	0.657
IV	20.00	50	21.70 †	0.0314	0.031	0.538
V	10.00	50	28.20 ‡	0.0134	0.022	0.381
		Isoamyl alcohol				
VI	39.36	50	10.64	0.0680	0.044	
VII	31.40	50	16.10 §	0.0520	0.042	

* + 3.60 cc. N/100 $AlCl_3$.
† + 8.30 cc. N/100 $AlCl_3$.
‡ + 11.80 cc. N/100 $AlCl_3$.
§ + 2.50 cc. N/100 $AlCl_3$.

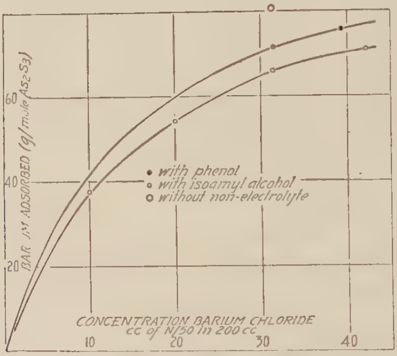

Fig. 4.

of phenol. It will be noted that the adsorption is cut down almost 20 per cent. This cutting down of the adsorption is not due to the very low concentration of aluminum ion (0.0018 N) since there is very little if any antagonistic action under these conditions. Similar results were obtained with isoamyl alcohol as shown by experiments VI and VII.

Comparing experiment III with VII, it will be noted that the adsorption of barium at the precipitation value of $BaCl_2$ in the presence of phenol is less than that in the presence of isoamyl alcohol. This indicates that phenol has sensitized the sol more than the alcohol, a result that might be expected from a comparison of the dielectric constants of the two compounds. It should be pointed out, however, that the concentration of phenol is higher than that of the alcohol; moreover, we have no measure of the relative adsorbability of the two non-electrolytes by the colloidal particles. One compound that is strongly adsorbed may have a greater effect than the same concentration of another compound having a higher dielectric constant, that is, less strongly adsorbed.

Attention should be called to Fig. 4 which shows that the adsorption of barium *below* the precipitation concentration follows the well-known adsorption isotherm. Such a result was predicted by Freundlich and was indicated by some earlier observations of the author.[57]

As already noted the precipitation value of potassium chloride is lowered quite appreciably by the presence of phenol. As Freundlich pointed out [58] this is probably due to the relatively flat character of the adsorption isotherm for univalent precipitating ions. With such ions the change in adsorption is usually very slight for relatively large changes in concentration; conversely, a slight decrease in the adsorption necessary for lowering the charge on the particles below the critical value will be marked by an appreciable lowering of the precipitation value. Thus a lowering of 10 per cent in the amount that must be adsorbed, such as observed in the preceding experiment, may cause a lowering in the precipitation value of 50 per cent or more, if no other factors enter in. As a matter of fact, the presence of phenol doubtless cuts down the adsorption of potassium ion,[*] a circumstance that would tend to increase the precipitation value. This effect is of course much less marked than in the case of barium chloride since the concentration of potassium ion is approximately 100 times greater than that of barium ion. Moreover, the high precipitation value of potassium chloride results, in part, from the fact that the adsorption of chloride ion at certain concentrations, is comparable to that of potassium ion.[59] Since the presence of phenol doubtless cuts down the adsorption of chloride ion as much or more than that of potassium ion, this amounts to a sensitization of the sol and a consequent decrease in the precipitation value. With barium chloride as precipitant, the concentration of the relatively slightly adsorbed chloride ion at the precipitation value is too low to have any appreciable influence.

We may now consider what will be the influence of a like amount of phenol or isoamyl alcohol on the precipitation value of a salt with a trivalent precipitating ion such as aluminum chloride. On account of the steep slope of the adsorption isotherm for aluminum ion as compared with that of a univalent ion, one should expect the small sensitization of the sol to lower the precipitation value but slightly.[60] Opposing this, is the cutting down of the adsorption of aluminum ion by adsorbed non-electrolyte. This latter effect should also be small on account of the very strong adsorption of aluminum ion even in low concentration. The sum of these two opposing influences would be expected to give a net change in the precipitation value that is very slight or negligible. This is in accord with experimental observations on several different sols and on several concentrations of the same sol. For more concentrated sols the difference in precipitation value of aluminum salts is too small to be detected; while for very dilute sols the precipitation value appears to be increased slightly in the presence of phenol. Since the concentration of aluminum ion necessary for precipitation is so low and the adsorption so great, the amount that remains in solution after precipitation is, unfortunately, too small to detect the very slight difference in adsorption that must exist in the presence and the absence of non-electrolytes.

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[*] According to Lachs and Michaelis (*Kolloid Z.*, **9**, 275 (1911)), the adsorption of chloride ion from solution by charcoal is not changed appreciably by the presence of phenol or isoamyl alcohol. On account of the high precipitation value of potassium chloride and the relatively small change in concentration of potassium ion after precipitation of arsenious sulfide sol, it was impossible to determine accurately the adsorption of potassium ion in the presence and the absence of non-electrolytes.

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Some Novel Aspects of Colloidal Protection

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Knowledge is like a steadily rising tide. We must keep continually advancing with it to ever higher and higher levels, or we will be surely overwhelmed, and perhaps with surprising swiftness; for with new developments in science, the tide sometimes rises with great rapidity. How eloquent was the example of Sir William Thomson (Lord Kelvin), who, after retiring at the age limit of seventy from the position of Rector of the University where for decades he had served with distinction, immediately matriculated there as a student.

Orthodox and unquestioned assumptions often break down, and old experimental data develop new facets when illuminated from a different angle. There are many, however, who, because of mental or intellectual inertia, resist the acceptance of truths inconsistent or apparently inconsistent with previously accepted or "classical" ideas of science, and like Procrustes of old, try to force newly-come facts to fit existing theories. Even some teachers of chemistry look askance at data or views which do not easily fit into the already sufficiently numerous and complicated laws and principles which they must make plain to the coming generation.

The practical man, unhandicapped by prior knowledge of what he ought to see and what it is unorthodox to observe, frequently makes discoveries that are far in advance of theoretical or scientific knowledge. Of course the *percentage* success of the practical man is far below that of the scientifically trained man; but tremendous *numerical* superiority and close daily contact with the practical problems of life, enable practical men, *in the aggregate,* to score a very large number of successful hits.

The purple of Cassius was regarded by Berzelius to be a definite chemical compound, for on precipitation and re-solution it acted as a unit; and for many years it was so accepted. About twenty-five years ago, however, Zsigmondy proved it to be an adsorption compound; he synthesized it by simply mixing colloidal gold and colloidal stannic acid; and just recently A. Huber [1] confirmed Zsigmondy's proof by X-ray analysis, which showed that none of the gold is chemically combined with the tin.

The technical use of what we now call "protective colloids" goes way back into the dim mists of antiquity, *e.g.,* in Chinese and India ink. The Chinese used glue in the manufacture of their ink to deflocculate the lamp-black, just as they also used sheeps' thyroids to aid morons—both worked. And the ancient Egyptians used gum (probably acacia) in their inks for the same reason, and made their clay as workable as that of Babylonia by the use of infusions of straw (see Exodus 5).

Continually, throughout chemical literature, the use of protective substances crops up, only to be buried again or to be hidden in the oubliette of some rule of thumb formula. The alchemists of the Middle Ages produced their *aurum* *potabile* by reducing solutions of gold in the presence of stabilizing ethereal oils; and at least as early as 1794 silk was dyed with colloidal gold. Berzelius' *Lehrbuch* (1844) gives recipes for producing several shades of colloidal gold, and long prior to this (in 1821) isinglass, egg albumen, and starch were used for the same purpose. Graham also recognized protective action in the case of caramel, regarding which he said:[2] "The presence of sugar and of the intermediate brown substances, protects the liquid caramel in a remarkable degree from the action of crystalloids and accounts for the preceding properties not being observed in crude caramel." These remarks refer to dialyzed caramel, which is extremely sensitive to crystalloids, and is pectized by traces of mineral acids, alkali salts, etc.

In 1897, just before Zsigmondy,[3] unaware of Faraday's earlier (Phil. Trans. 1857, p. 145) work with "jelly" (evidently isinglass or gelatin) as a protector for colloidal gold, had independently rediscovered the phenomena, von Meyer and Lottermoser [4] recognized protective action as such. They drew attention to the fact that albumin stabilizes silver sols—a fact well known to practical photographers. In his book "Anorganische Kolloide," p. 50 (1901), Lottermoser said: "On the addition of very stable colloids, as albumin, gelatin, agar, or gum arabic, to a silver sol, no precipitation is caused by electrolytes until the stable colloid is coagulated. The less stable silver sol is thus protected against the electrolyte by the more stable colloid; it becomes more like it in its behavior."

A most important contribution of Zsigmondy, however, was his demonstration that stable though highly sensitive gold sols could be made without the use of protectors, providing the presence of coagulators was avoided, and the proof that these sensitive sols could be stabilized by the addition of gelatin, gum and the like. Then only was it that the full import of colloidal protection began to dawn, and the use of the principle, as such, begin to be understood and developed.

Broadly speaking, a protector is a substance that opposes the aggregation of molecules or particles into larger groups. In general the so-called emulsoid colloids (*e.g.*, gelatin, albumin, soaps, gum arabic) act as protectors to hydrosols; but citrates, tartrates and other substances commonly thought of as crystalloids may also serve as protectors. Naturally findings on hydrosols do not apply to sols with a non-aqueous dispersion medium. Frequently protectors also serve as dispersers, peptizers, or deflocculators, but may not then yield as fine a dispersion as could be obtained by preventing the aggregation of particles *ab initio*.

It is natural to expect that substances will vary widely in their protective power, if indeed they show any protective action at all; and also that a substance which is a protector in one set of conditions may, under other conditions, show a different degree of protective action, or none at all. To establish some measure of protective action, Zsigmondy determined the number of milligrams of protective substance which would just fail to prevent 10 cc. of pure colloidal gold solution from changing its color from red to violet upon the addition of 1 cc. of 10 per cent sodium chloride solution. These ruby-red gold sols contain 0.005-0.006 per cent of gold, and are exceedingly sensitive to traces of electrolytes. The subjoined table gives such "gold numbers" for a variety of substances, taken from the results of Zsigmondy and of Schryver.

The results with sodium stearate indicate that the degree of dispersion of the protector is a very material factor in its action, just as it is in the detergent value of soap, and lends support to the generally accepted view of Bechhold [5]

Substance	Gold Number
Gelatin	0.005–0.01
Russian glue	0.005–0.01
Isinglass	0.01–0.02
Casein (in ammonia)	0.01
Egg-globulin	0.02–0.05
Ovomucoid	0.04–0.08
Glycoprotein	0.05–0.10
Amorphous egg-albumin	0.03–0.06
Crystallized egg-albumin	2.00–8.00
Fresh egg-white	0.08–0.15
Gum arabic	0.50–4.00
Gum tragacanth	2.00 ±
Dextrin	6.00–20.00
Wheat starch	5.00 ±
Potato starch	25.00 ±
Sodium oleate	0.40–1.00
Sodium stearate at 100 degrees	0.01
Sodium stearate at 60 degrees	10.00
Deutero-albumose	∞
Cane sugar	∞
Urea	∞
Stannic acid sol (old)	∞

that protective action is consequent upon the adsorption of a layer of the protector at the interface between the dispersed and the dispersing phase. The thinness of the layer seems obvious from the fact that Zsigmondy (who supports Bechhold's view) could see no diminution of the Brownian motion caused by it, nor any ultramicroscopic evidence of its existence. Since protectors are substances having considerable attraction for water and as a rule a great swelling capacity, it is not unlikely that even after ordinary desiccation they may swell enough to force the constituent particles of the protected substance far enough apart so that they are beyond the range of molecular attractive forces which is ordinarily estimated to be about 50 μμ.

Zsigmondy, following W. B. Hardy, classified colloid sols into two broad classes, based on their behavior on desiccation at ordinary temperatures—the reversible or resoluble, and the irreversible or irresoluble sols. These correspond roughly with the groups hydrophile/hydrophobe (Freundlich) lyophile/lyophobe (Perrin), and suspensoid/emulsoid (Wo. Ostwald). Although some salts (citrates, sulphocyanates) may act as protectors, protection is generally accomplished by adding a reversible or emulsoid colloid to an irreversible one which thereupon acquires reversible properties; that is it becomes insensitive to electrolytes, redissolves after desiccation (at any temperature that does not render the protector insoluble) and passes through ultrafilters that would otherwise hold it back.

Experimentally it is a most surprising fact that certain minimal quantities of protectors actually sensitize instead of protecting, and may themselves even produce flocculation. Thus according to Bechhold,[6] 0.0003 to 0.0001 per cent of gelatin per million will flocculate gold sols or oil emulsions. The work of J. Billiter[7] indicates that this is due to the fact that in such cases the minute amount of added protector brings the other colloid to or near the isoelectric point, where as Hardy has shown, all colloids are especially susceptible to coagulation.*

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* We may understand immunity as due to an antigen which has gradually, by selective adsorption, surrounded itself with a protective colloidal layer of sufficient quantity and quality that it may take up and render harmless a succeeding quantity of antigen, or else insure its agglomeration as a colloidal sol. Thus the ultramicroscope shows that tetanus toxin and tetanus antitoxin mutually

From what has been said it is evident that although in general, oppositely charged colloids precipitate each other, if an excess of a positive protective reversible emulsoid sol be quickly added to a negative irreversible (suspensoid) sol, the protector is adsorbed and protects before precipitation can occur. If, however, only a very small quantity of the protector is used, or what amounts practically to the same thing if the protector be added very slowly, precipitation may occur before protection can be established. That is precipitation may depend upon the speed of mixing as well as on the relative proportions mixed. This gives us also an explanation of the curious "zones of precipitation" investigated by Neisser and Friedemann, H. Bechhold, Teague and Buxton, A. Lottermoser, and J. Biltz.*

It is not at all strange that the behavior of a sol should be in large measure controlled by the nature of the outer layer or skin of its particles. Adhesion, as is well known, depends upon the nature of the outside layers, and so in fact does chemical action; for while the nucleus of an elemental atom is mainly responsible for its atomic weight, its chemical behavior is governed by its outer ring or layer of electrons.

It would be a long task to discuss the numerous cases where colloids are used, wittingly or unwittingly, in scientific, medical, or technical practise, as protectors, deflocculators and emulsifiers, or where they must be removed because their presence is detrimental. Problems of this kind abound in such widely diverse fields as photography, metallurgy, brewing, rubber, paper, glass, filtration, cooking, cement, agriculture, tanning, paints, pharmacy, biology, etc. Colloidal sols exist everywhere in the organism, and no reaction takes place there without being influenced by their presence.

To illustrate the working of protection just compare precipitates of silver chloride and tin or lead "trees" made in the presence of, and in the absence of gelatin. Or divide a lead acetate solution into three parts, adding a little hot gelatin solution to the last. The first will give with hydrochloric acid a curdy precipitate of lead chloride; the second will give with sodium chloride (which is less highly ionized than HCl) a turbid lead chloride sol; while the gelatin containing solution will, preliminarily at least, show no visible turbidity with sodium chloride.

A capital instance of the effect of colloidal protection is seen in the case of milk, where the casein, an unstable colloid, is protected or stabilized by lactalbumin. In the older books this relation of the two proteins was obscured by the practise of reporting their sum as "total proteids"; but the following table, based on the averages of Koenig, at once shows the great differences between mils, as well as the importance of the casein/lactalbumin ratio in determining these differences.

AVERAGE COMPOSITION OF VARIOUS MILKS

Kind	Casein	Lactalbumin	Fat	Lactose	Protective Ratio
Cow	3.02	0.53	3.64	4.88	0.175
Woman	1.03	1.26	3.78	6.21	1.22
Goat	3.20	1.09	4.78	4.46	0.34
Ewe	4.97	1.55	6.86	4.91	0.31
Mare	1.24	0.75	1.21	5.67	0.605
Ass	0.67	1.55	1.64	5.99	2.31

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precipitate each other, as do diphtheria toxin and antitoxin.[8] Where the adsorbed protective layer is deficient in quantity or quality, we may have a hypersensitisation to precipitation, so that a small succeeding dose of antigen produces a coagulation in masses sufficiently large to cause embolism. In this manner we can understand the condition known as anaphylaxis and its occasional consequence, anaphylactic shock.

* See paper by A. Lottermoser, this volume, p. 670.

Experiment shows that cows' milk is much more readily coagulated by acid and by rennin than is mothers' milk, and that the coagula of mothers' milk if formed, are much finer. The addition of *any* protector—proteins like gelatin or albumin, carbohydrates like dextrin, Irish moss, or gum arabic, or even salts like sodium citrate—will make cows' milk behave more like mothers' milk, and will make it more digestible for the infant. Regarding the highly protected asses' milk so eminent an authority as A. Jacobi stated as far back as 1888 that it is a refuge to which the physician flies when neither cows' milk nor even mothers' milk is tolerated.*

Plural Protection

An outcome of these observations on milk was the development of the idea of *double or plural protection.* The attempt to produce an imitation of casein by forming a precipitate of calcium phosphate in the presence of protectors (gelatin, gum arabic) was not fruitful when the protector was added to the phosphate solution or to the calcium solution. On reflection, however, it was evident that in the organism *both* of the reacting solutions contain protectors, and on protecting both the sodium phosphate and the calcium chloride, there was obtained a colloidal calcium phosphate which could be precipitated by acid or by rennin. Olive oil was emulsified in this and a stable imitation milk was obtained. Thus was developed the principle of double and plural protection, for which a U. S. Patent was secured.

The literature contains several instances where this principle has been used in a more or less empirical manner. Thus Carey Lea produced some of his colloidal silver by the following formula:

Solution 1		Solution 2	
Water	800 c.c.	Water	800 c.c.
20 per cent Rochelle salt solution	200 c.c.	20 per cent Rochelle salt solution	200 c.c.
40 per cent silver nitrate solution	50 c.c.	30 per cent cryst. ferrous sulphate solution	107 c.c.

Solution 2 was then added to solution 1. The Rochelle salt here acts as a protector.

In the photographic field the so-called Lippmann "grainless" emulsion is made by the following formula:

Solution 1		Solution 2	
Gelatin	75 grains	Gelatin	75 grains
Potassium bromide	32 grains	Water	8 oz.
Water	8 oz.	Silver nitrate	45 grains

The ingredients are mixed in the order given; and after allowing the gelatin to swell, the solutions are heated to 95 degrees F. Then solution 2 is added to solution 1.

And Lobry de Bruyn [9] found that, upon adding gelatin to both reacting solutions precipitation may in many cases be inhibited, a colloidal dispersion resulting. Thus under these conditions potassium bichromate and silver nitrate give a brick red coloration but no precipitate. In general Lobry de Bruyn used tenth to twentieth normal solutions, protecting them with 5 to 10 per cent of gelatin.

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* In this connection it seems possible that any cause which decreases the proportion of lactalbumin to casein in mothers' milk—nervous shock, anemia, etc.—may tend to register itself in a digestive upset in the nursing infant. This ratio undoubtedly varies with the period of lactation as well as in different cows, so that the milk of a herd is probably much more uniform than that of one cow.

The value of this principle in technology is obvious, and in medicine and in bio-chemistry it must be of exceedingly great importance, for in the organism all reacting solutions are protected. The work of Auguste Lumière and others has shown the disastrous consequences that follow the formation of flocculates of sufficient size to cause nerve irritation, capillary embolism, and the wide variety of symptoms which may follow more or less directly or indirectly from the appearance in the blood stream of particles of unusual dimensions. In addition protectors very generally lead to the formation of crypto-crystalline structures, obviating sharp crystalline deposits.

INFLUENCE OF COLLOIDS ON CRYSTALLIZATION

Protective substances exert a very marked effect on crystallization and crystalline form. We are all familiar with the beautiful ice tracery on window-panes, some of which involves this phenomenon; and a mixture of epsom salt ($MgSO_4$) and beer or other colloid-containing binder is often used to produce fern-like figures on glass, paper, etc. Some neglected work in this field recently brought to light[10] is that of Dr. Wm. M. Ord[11] and his immediate predecessors, including Mr. George Rainy, who perhaps working under the influence of Graham, realized the biological importance of this phenomenon. Quite independently, J. Alexander[12] rediscovered it in connection with investigations of the function of gelatin (and other protective colloids) in ice cream. Alexander found that such protectors inhibited the formation of sharp ice crystals * and give the ice cream a smooth velvety taste From what has been said above relative to milk, it is obvious that protectors tend also to render milk and ice cream more readily digestible.[13]

The crystal-inhibiting action of protectors is well illustrated by plaster-of-Paris, in which they are used as "retarders," to delay the time of setting. The following table of results is interesting:

One Part Water Containing Gelatin—Per Cent	Time to Set in Minutes	Microscopic Appearance of Slide
0	40	Characteristic crystals of calcium sulphate.
1/100	50	No crystals, except in a few spots where some colloid-free solution had diffused out.
1/10	260	No crystals.*
1/4	510	No crystals.*
1/2	960	No crystals.*
1	Not set in 48 hr.	No crystals.*
2	Not set in 48 hr.	No crystals.*

* No regular, ordinary crystals, the mass consisting of aborted, modified or sphero-crystals, or of colloidal crystals or other minute unoriented groups, or of a mixture of these.

In metals and alloys and in electroplating, the inhibition of crystal development is of great technical importance. (See Vol. III.)

AUTOPROTECTION

Since every substance, in the course of aggregating from atomic or molecular dispersion into visible masses, must of necessity have in it at some time particles of colloidal dimensions, we must face the condition known as *iso-colloidism,* wherein the colloidal dispersion of the substance is in contact with a non-colloidal phase of the same substance. If the colloidal phase has the property of being adsorbed or of adsorbing, we may have *autoprotection*, where the substance delays or prevents its own crystallization. The work of Quincke, O. Lehmann, and others indicates that crystal formation is preceded by the formation of tiny globulites, and by rapid evaporation of a film of a solution of sulphur in carbon disulfide containing a little Canada balsam to slow down the aggregation process, these globulites and their various stages of aggregation may be seen.[14] An analogous adsorption seems to delay the transformation of γ-iron into α-iron (allocolloidism), and it is especially observable in ammonium salts and in soaps, *e.g.*, in oleates.

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* This must not be confounded with the sandiness due to formation of lactose crystals in ice cream mixes containing *condensed* milk.

In the case of solutions, where the viscosity is not too great, the autoprotective stage is of limited life.

W. B. Hardy[15] found that 5-dimethylaminoanilino-3-4-diphenylcyclo-1-2 dione upon cooling from its solutions in organic solvents gives gels that gradually become crystalline. Gortner and Hoffmann[16] report that dibenzoyl-1-cystine forms even in 0.2 per cent solution a rigid gel which in the course of several weeks crystallizes almost completely. So powerful is its gelatinization that this dilute solution makes as strong a jelly as a five per cent solution of gelatin. Camphorylphenylthiosemicarbazide acts similarly, its solutions in organic solvents forming on quick cooling, gels that gradually become crystalline.[17]

CUMULATIVE PROTECTION

The general rule in colloidal protection is that anything which removes, coagulates, or destroys the protector, or disperses it crystalloidly, will tend to cause the protected dispersion to coagulate. Thus on adding ferric chloride to olive oil emulsified with gum arabic, the gum is coagulated and loses its emulsostatic action, so that the oil separates out—the emulsion "breaks." On the other hand, anything that protects the protector, that is, stabilizes it against coagulation, crystalloidal dispersion, or destruction, will tend to stabilize the protected sol. Thus some ammonia in a gelatin-protected sol would tend to prevent the coagulation of the gelatin by formaldehyde, and an antiseptic would prevent its dispersion by bacteria or enzymes which, as the work of E. Zunz[18] indicates, may convert protectors into coagulants. The rennin coagulation of milk seems to be of this nature, the enzymes converting the protective lactalbumin into a coagulant.[19]

This introduces a new idea—*cumulative protection*. In many cases we must expect to find that the protector of the protective colloid is itself a colloid, and there is no reason to doubt that cumulative protection may extend through a series of several colloids, or colloids and crystalloids, giving a structure which like a house of cards, may collapse if any one of its essential supports is removed.

This aspect of protection does not seem to have been recognized or investigated experimentally as such, and it offers a wide field for research. As instances of its practical operation may be mentioned glasses, alloys, and the gluten of wheat and rye flours. Many protein and similar complexes may be built up in this fashion.

The inherent tendency of glass toward crystallization often leads to *devitrification*, a phenomenon in which relatively large crystals are formed, rendering the glass turbid and unworkable. Some silicates may be cooled slowly without crystallizing (apparently because of isocolloidism resulting in auto-protection), but the silicates of calcium, magnesium, and aluminum form crystals if not quickly chilled, an accomplishment difficult of realization because silicates combine high thermal capacity with low thermal conductivity.

In the course of crystallization from crystalloidal dispersion, every substance must of necessity pass through a zone where many of its particles are in a colloidal degree of dispersion,[20] and in this zone, even though it be a transient one, surface forces (adsorption, surface tension) exercise a dominant influence. The tendency of various silicates to adsorb each other as they reach colloidal dimensions introduces a *time lag* in the process of crystallization. This time lag becomes cumulative as the several silicates adsorb and protect each other; and is naturally enhanced as the viscosity of the whole mass increases. The glass technologist chooses the proportions of his batch so that the protective action of the alkali silicates and other protectors will be amply sufficient to inhibit crystallization (devitrification) over the range of mechanical and thermal treatment to which the batch is to be subjected. In addition the mechanical and chemical properties of the glass must be considered, so that protection is often accomplished by a mixture of diverse ingredients, some of which may be present in very small quantities, and yet, because of the principle of cumulative protection, exercise a potent effect.

Tammann [21] named as the three main factors controlling the behavior of supercooled melts (1) the *specific crystallization capacity* (measured by the number of centers of crystallization formed in a unit mass in a unit time); (2) *the speed of crystallization;* (3) *the variation in viscosity.* From what has been said it seems that it is evident that in mixtures there must be added a fourth factor—*cumulative protection.* These four factors are closely interrelated.

Alloys also are examples of mixed supercooled melts, and in them, as in glasses, we find evidence of cumulative protection, to which may in large measure be attributed the structure of many seemingly complicated alloys such as high speed steels, duraluminum, etc., where some of the numerous ingredients are present in small quantities. The behavior of some alloys is further complicated by *allocolloidism,* leading to auto-protection; thus in steel we must reckon with the fact that iron exists in at least two allotropic forms.[22]

In considering the gluten of wheat and rye flours, it must be remembered that the various gluten fractions can hardly be definite chemical individuals, but probably are adsorption groups of fairly uniform composition. The principal fractions are:

Glutenin, insoluble in water or dilute saline solutions, soluble in dilute acid or alkali, but precipitates upon neutralization.

Gliadin, yields a colloidal opalescent solution with distilled water, from which sodium chloride precipitates it.

Globulin and Albumin, soluble in sodium chloride solutions.

In a complex colloidal system of this character, salts, up to certain concentrations, will enhance the protective action of the globulin and albumin, but decreases that of the glutenin and gliadin, which are in fact rendered more susceptible to assuming the coagulated or gel-like condition essential to making a satisfactory dough. Salts occur in the flour itself and in the water used, which has in baking an importance similar to that which it exercises in brewing. Furthermore ordinary salt has been used in bread making from time immemorial, and besides rendering the bread more palatable, exercises an important function in regulating the behavior of the gluten. Too much salt is fatal, for as Weyl and Bischoff found, flour moistened with a 15 per cent solution of sodium chloride will not make a dough. Neither will flour which has been heated for several hours at 60° C., probably because of the excessive dehydration of one or more of the constituent colloids of the gluten; even gelatin becomes insoluble if heated to 110 degrees or more.

The effective reaction of the dough mixture (as measured by the H ion concentration or p_H value) must also materially affect its body. Slight acidity or alkalinity will solubilize the glutenin. Soft alkaline waters disintegrate the gluten and destroy its elasticity, whereas hard waters containing sulphate of calcium, etc., tend to harden it. Yeast develops a slight acidity which affects the body of the dough, and in turn the yeast is affected by the salts present. Such *yeast foods* as potassium bromate, register an effect upon the physical condition of the glutenin. The colloid chemical behavior of flours, having in mind cumulative protection, offers a most fruitful field for research.

H. Freundlich and H. J. Kores[23] found that dilute solutions of pure sodium oleate or of pure sodium stearate have a low viscosity, but that mixtures have greatly increased viscosity, in some cases six to forty times as great. The maintenance of a marked colloidal degree of aggregation was evidenced by the appearance, in the ultramicroscope, of long threads. From this we may surmise that the behavior of very highly purified material (*e.g.*, fats, soaps, metals) will be noticeably different from that of commercially or even ordinarily "chemically pure" substances. The startling results of Prof. H. B. Baker,[24] who raised the boiling points of quite a variety of substances from 15 to 60° C. above these boiling points accepted as correct for the chemically pure materials, shows the potent effect of even traces of impurities. On removing the last traces of moisture from "absolute alcohol," he found that its boiling point went up to about 138° C., a rise of 60° C.

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Fibrous Alumina

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Fibrous alumina is worthy of particular attention as an inorganic gel of remarkable properties, (1) because of its individual *mode of formation*, (2) its resultant *structure* (macroscopic, microscopic, and ultramicroscopic), (3) its characteristic *surface reactions* due to this structure, (4) the amphoteric nature of the aluminium oxides and aluminium hydroxide.

The mode of formation, structure, and reaction of fibrous alumina constitute an important "topochemical" † phenomenon, because this material is in almost every respect the artificial analogue of fibers developed in the living organism. The author, therefore, originally called the phenomena "grown alumina." It "grows" almost exactly like natural fibers. The analogy is not quite precise, but it is nevertheless an extraordinarily illuminating one for the colloid chemistry of the structure and properties of cell-membranes and fiber development as a whole.

The actual chemistry of its mode of formation is as follows:

(1) Al_n (metallic) $+ 3HOH \longrightarrow Al(OH)_3 + 3H + Al_{n-1}$ (metallic)
(2) $Al(OH)_3 \longrightarrow AlO(OH)_2 + HOH$
(3) $2Al(OH)_3 \longrightarrow Al_2O(OH)_4 + HOH$
(4) $2Al(OH)_3 \longrightarrow Al_2O_3 + 3HOH$

According to these chemical equations, metallic aluminium undergoes various steps in hydration, resulting in aluminium oxide, which correspond to the natural mineral "hydragillite," "diaspor," and chemical intermediate steps of dehydration, and through intra- and extra-molecular splitting off of water, $Al(OH)_3$ becomes the fully dehydrated Al_2O_3.

Aluminium, as a base earth metal, is especially capable of such a spontaneous reaction. Because of the great avidity of aluminium for oxygen, its very high heat of oxidation would complete the reaction very speedily if the heat were not allowed to dissipate quickly. Every clean surface of compact metallic aluminium is covered with a transparent molecular skin of aluminium oxyhydrate. In a checked reaction, firstly the hydrogen escapes, and with it the "molecular" film of water incidentally condensed on the surface. The expansion and escape of this gas results in a cooling of the metallic surface and the gel skin. The cooling and the adsorption of water in the highly dispersed membrane lead to a concentration and adhesion of the skin, which brings the reaction to a standstill. The gel skin *mechanically* separated from the metal surface is extremely hard; it can be *chemically* separated readily with caustic soda. But the clean metal surface is soon covered with a new thin skin, which again interrupts the reaction. There is, however, a method of allowing the reaction to continue by means of a catalytic agent -the contact of mercury with a surface of metallic aluminium, preferably chemically cleaned and with as large a surface as possible. The best form of the metal was found by the author to be granular aluminium "grits." The reaction takes place best when the surface is attacked by caustic soda, quickly and repeatedly washed off with a powerful water-spray, a small amount of $HgCl_2$ solution being added, followed by renewed washing with water. All told, it is best to repeat this chemical technique after the last washing with water, and finally to wash with alcohol. With great development of heat, voluminous "fibrous alumina" is formed in an aggregated mass as finely powdered dispersed alumina; but here and there on individual granules of "activated aluminium" there is also formed large-fibered fibrous alumina; both with the greatest amount of free surface and adsorptive power.

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* Translated by Eleanor G. Alexander, B.A.

† This term was originated by Kohlschütter, and indicates the dependence of external structure on specific reaction conditions.

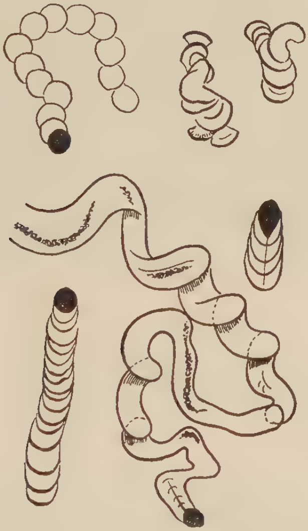

FIG. 1.—Formation of cell membranes and fibers on grains of activated aluminium (according to microscopic observations of L. Jost).

This catalyzed reaction can be expressed by the equation:

$$(5)\quad [Al(Hg)]_n + 3nHOH \longrightarrow [Al(OH)_3]_n \text{ fibrous} + 3nH.$$

It is meant to express the catalysis and the formative or topochemical process.

The compressed hydrogen quickly inflates the alumina skin until it tears and again exposes the active free surface. Gas pressure is thus the most potent form-giving factor, whereas organic membranes grow slowly and are formed over protoplasm by osmotic pressure.

The formation and structural characteristics are explained in the following Plate.[1] Fig. 1 gives a microscopic picture of the growth of $Al(OH)_3$-cell pellicles and fibers grown from pieces snipped off of aluminium wire, which have been activated by Hg. According to the shape of the various pieces of wire, variously formed membranes grew under the microscope. From round pieces of metal there grew rows of spherical cells, from oval or pointed pieces, elongated membranous cell structures, mostly intergrown. Rapid "growth" produces long-drawn-out fibers with the morphological characteristics of natural organic fibers. The granules of activated aluminium thus arrange themselves in a way similar to the way protoplasts of the living plant and animal cell are arranged in colloidal cellulose fibers and membranes. (Figs. 2-3.) As in all natural fiber-structures, fibrils or micells, thick and thin, sheathed in the finest of thin pellicles appear here and there in the "anisotropic" arrangement of the crystallites, which causes a double refraction of polarized light as do organic fibers. Fig. 4 illustrates such a condition, and Figs. 5 and 6 show again the similarity between artificial aluminium fibers and natural cotton resolved almost ultramicroscopically.

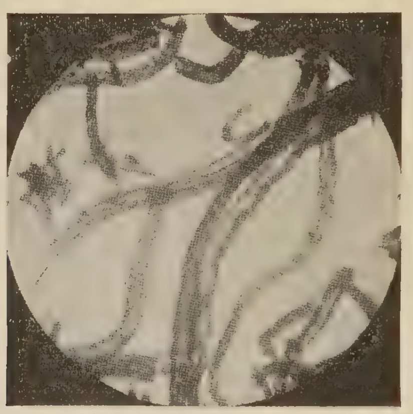

Fig. 2.—Fibrous alumina, × 50 ±.

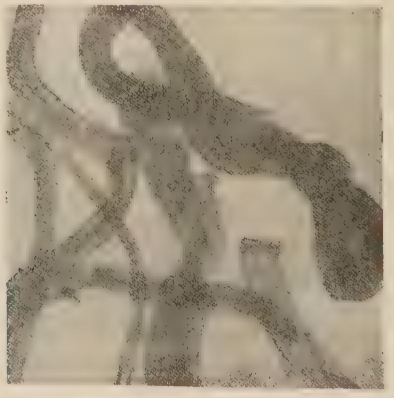

Fig. 3.—Cotton (after Kirchner).

In "grown" fibers we have solid substance in a profoundly dispersed condition; they are, therefore, ideal adsorbents. In comparison with other well known adsorbents (hide-powder; bone, blood or wood charcoal) fibrous alumina has shown a far higher degree of adsorptivity for tannin, congo-red, and tanning substances.[2] They adsorb tannin from a 0.3 to 0.5 per cent solution to 50 per cent of their own weight, and from a 0.1 per cent solution of congo-red up to 5 per cent of its own weight. Attempts to obtain dispersed alumina in other ways[3] ("swollen or inflated alumina") have shown that such alumina shows inferior adsorption.

Recently, *Willstätter* in Munich, and *Kohlschütter* in Bern have reported experiments on the manufacture of dispersed aluminium hydroxide. Similar attempts were made, originally at the author's suggestion, by the chemical factory of Heyden & Co. in Radebeul near Dresden, in order to investigate thoroughly and apply the extraordinary ability of the hydrogel $Al(OH)_3$ to become *very* highly dispersed. The above named authors used chemical precipitation methods; *Kohlschütter,* in order to study topochemical reactions, and *Willstätter,* in order to use dispersed aluminium hydroxide in the separation of ferments by adsorption.* The forms of aluminium hydroxide produced by *Willstätter, Kohlschütter,* and *Heyden & Co.* do not reach the highly dispersed condition of fibrous alumina, and therefore did not exhibit the degree of surface activity shown by "grown" alumina fibers. Since in its

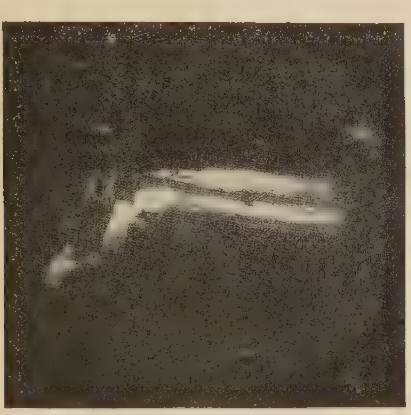

FIG. 4.—Fibrous alumina exhibiting double refraction in the polarization microscope.

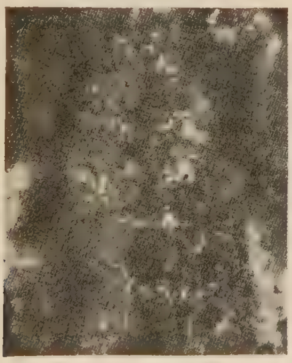

FIG. 5.—Fibrous alumina, × 450 in oblique illumination (almost ultramicroscopic).

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* See paper by R. Willstätter, to appear in Vol. II. J. A.

gross solid state alumina is extremely compact, it seems in order to call this condition a profoundly dispersed solid state.

In natural structures of this class (cell-membranes, plant and animal fibers) this is responsible for characteristic reactions which, especially with supporting substances (cellulose fiber, etc.), are necessary for the growth and life of the vegetable organism; for these complicated, insoluble, chemically inert supporting substances, while without internal chemical change, react by adsorption with concentrated as well as with dilute growth-producing substances.

Alumina fibers differ in certain important properties from natural fibers. A nonvolatile inorganic substance like $Al(OH)_3$ fibers can be completely freed of water by thorough heating, without loss of structure and adsorptivity. The correspondingly lessened weight of the oxide still possesses the same surface attraction and adsorbtivity as the larger mass of oxyhydrate from which it was obtained. When heated too strongly sintering causes the loss of some of the surface and surface reaction of the delicate fiber mass. Therefore an absolutely dehydrated determined quantity of absorbent may be used in analysis. The fact that the *pure white color* characterizes both the hydrate and the oxide fibers means that any colored adsorbed substance can be qualitatively recognized (dyes, tanning material, etc.). Color reactions on colorless adsorbents can thus be carried out meticulously, the carbon of organic adsorbed substances can be burnt off easily and quantitatively determined.

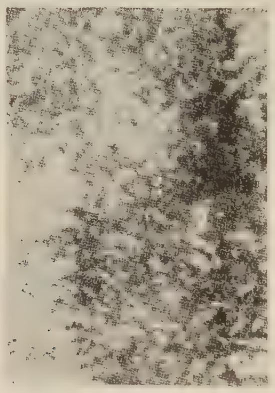

Fig. 6.—Cotton yarn, dyed; ultramicroscopic picture of Gaidukov.

Fibrous alumina as an adsorbent is obviously not sensitive to dampness and bacteria. It can, therefore, be used for the determination of tannin in a tropical as well as in a dry climate.

In tannin determination,[4] because of its amphoteric chemical nature, it is an ideal adsorbent, for its behavior is remarkably like that of hide fibers.[5] It differs greatly in physical properties from all organic fibers. Fibrous alumina is very *brittle* whereas most organic fibers possess extraordinary elasticity. The difference, however, is only one of degree, for fibrous alumina possesses a small amount of elasticity. Larger well-developed alumina fibers break readily, but only when the accumulated masses are "blockaded"—that is, demand much more space than would a solid powder of alumina not "grown" in this way. Well-developed fibrous alumina has a sp. gr. of about 0.1;

that of a more concentrated aggregation around 0.33 to 0.4. Aluminium hydroxide which is not in the "grown" form has a sp. gr. of 1.2-1.5; the specific gravity is a criterion of quality.*

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* Fibrous alumina according to the author's methods is made by E. Merck in Darmstadt, Aarheilgen.

The Influence of Colloids on the Solubility of Gases

By Henry Jermain Maude Creighton,
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The question of the absorption or solubility of gases, more especially oxygen and carbon dioxide, in blood is one of essential importance and one which has claimed the attention of many physiologists. For a long time the purely chemical explanation of absorption was practically undisputed, the absorption of oxygen by blood being attributed mainly to the formation of a compound with hæmoglobin, and that of carbon dioxide to the reputed alkalinity of the blood and the formation of carbonates and bicarbonates. Later, however, Findlay and Harby[1] and Wo. Ostwald[2] suggested that the absorption might be due to the surface action of the colloids present in blood. This view was fully discussed by Wo. Ostwald[3] on the basis of the experimental data at that time available. Before this view could be tested, it was necessary to study the influence of colloids of various kinds on the solubility of gases. Accordingly, an extensive investigation was carried out by Findlay and his co-workers, the solubility of different gases being determined at pressures between 250 and 1400 mm. of mercury. In addition to its importance in relation to the absorption of gases by blood, the investigation is of interest in connection with the absorption of carbon dioxide by beer.

The influence of ferric hydroxide, gelatin, arsenious sulphide, silicic acid, starch, glycogen, egg albumen and serum albumen, as well as fine suspensions of charcoal and silica, on the solubility of carbon dioxide and nitrous oxide in water has been studied by Findlay and Creighton[4] at 25°, and at various pressures ranging between 750 and 1400 mm. of mercury. At atmospheric pressure silicic acid, charcoal and silica increase the solubility of both gases; gelatin and ferric hydroxide increase the solubility of carbon dioxide, but diminish that of nitrous oxide; the remaining colloids, with the exception of arsenious sulphide which is practically without influence, decrease the solubility of both carbon dioxide and nitrous oxide.

The following types of solubility-pressure curves were obtained: 1. Where the solubility is increased above that of the gas in pure water, then at higher pressures the solubility curve (a) remains nearly horizontal (*i.e.*, the solubility of the gas practically obeys Henry's law), or falls to a flat minimum (*e.g.*, carbon dioxide in the presence of silicic acid, ferric hydroxide, gelatin); (b) rises continuously (*e.g.*, carbon dioxide and nitrous oxide in the presence of charcoal and silica, and nitrous oxide in the presence of silicic acid). 2. Where the solubility is decreased below the water value, then at higher pressures the solubility curve may either rise continuously or, generally, fall to a minimum and then rise more or less steeply. For the ascending portion of all of the curves, the ratio C_2^4/C_1 is constant, C_1 and C_2 representing the concentration of the gas in the colloid phase and the solvent, respectively. The well defined minimum of solubility is more marked in concentrated than in dilute solutions. In all such cases the influence of the colloid must be a complex one, and two factors, at least, must come into play: one causing a decrease of solubility with rise in pressure, the other an increase. In dilute solutions the former is sometimes absent or negligible.

The cases under 1(a) are explained on the basis of chemical interaction; those under 1(b) on the basis of adsorption. The behavior in the cases under 2 probably depends on (i) solubility of the gases in a polymerized form in the colloid phase (descending portion of the curve), and (ii) adsorption (ascending portion of the curve).

General confirmation of the foregoing results has been obtained by Findlay and Williams [5] with carbon dioxide, and by Findlay and Howell [6] with nitrous oxide, at pressures between 250 and 760 mm. of mercury. They have also shown that the solubility of these gases in colloidal solutions is relatively high at low pressures, and that it decreases with increasing pressure either to a constant value, or to a minimum value, after which the solubility again increases with rising pressure.

Findlay and Shen [7] have found that the solubility of carbon dioxide in aqueous solutions of a number of inorganic salts and in aqueous solutions of sucrose and chloral hydrate is in harmony with Henry's law, thus proving that the behavior observed in the case of these solutions is different from that found in the case of colloidal solutions. They have also demonstrated that the solubility of carbon dioxide in aqueous solutions of peptone, propeptone and hæmoglobin is greater than in water, but that it decreases with rising pressure. This behavior is attributed to chemical combination. On the other hand, the solubility of hydrogen in aqueous solutions of dextrin, starch, gelatin and ferric hydroxide, and in a suspension of silver, is in accordance with Henry's law.

From the results that have been presented, it is evident that the influence of colloids on the solubility of gases is often complex. It is clear that the presence of a colloid in solution will not necessarily increase the solubility of a gas. The action is a specific one, and depends both on the colloid and on the gas.

The solubility of carbon dioxide, oxygen, carbon monoxide, nitrous oxide and nitrogen in ox blood and in ox serum at 25° has been measured by Findlay and Creighton [8] at pressures between 760 and 1400 mm. of mercury. The solubility of the first three gases in blood, and that of the first gas in serum, is much greater than in water; the solubility of nitrogen and nitrous oxide in blood and serum, and of oxygen and carbon monoxide in serum, is less than in water. Where the solubility is increased above the solubility in pure water, the solubility curves fall with increasing pressure. The increased absorption is probably due to the formation of chemical compounds. Where the solubility is diminished, the solubility curves rise with increasing pressure. Since the ratio C^n_2/C_1 (where n is greater than 2 and is usually 4) is constant for the rising portion of the solubility curve, the increased absorption with pressure is to be attributed to adsorption. Although several investigators [9] have obtained results which indicate that blood serum is "water-neutral," the results of this investigation strengthen the chemical explanation of the absorption of carbon dioxide by blood and are in harmony with the work of other experimenters.[10]

The results of Langer and Schultze's experiments on the absorption of carbon dioxide by beer [11] have been explained on the assumption that beer dissolves more of the gas than the corresponding water-alcohol mixture. Emslander and Freundlich [12] have attributed the supposed increase in solubility to adsorption of the carbon dioxide by the colloids present in beer. These conclusions, however, are not only not in harmony with the results obtained by Findlay and Creighton,[13] but Findlay and Shen [14] have shown that the gas is, as a matter of fact, less soluble in beer than in the corresponding water-alcohol solution. The contrary conclusion reached by Langer and Schultze must be attributed to their having employed beer supersaturated with carbon dioxide.

The influence of colloids and fine suspensions of charcoal on the velocity of evolution of carbon dioxide from well-agitated, supersaturated solutions has been determined by Findlay and King.[15] They have found that whereas, in the case of pure water and aqueous solutions of potassium chloride, the velocity of evolution of the gas is very nearly proportional to the degree of supersaturation, this is no longer true in the case of colloidal solutions, which show marked differences among themselves. Reduction of pressure is usually first followed by a period of quiescence, during which practically no gas is liberated. With solutions of ferric hydroxide and peptone, however, no such quiescent period occurs, spontaneous evolution of the gas taking place as soon as the pressure is reduced. Previous treatment of the colloidal solution, such as boiling, cooling, aging and the duration of the period of saturation with the gas, has an influence on the velocity of the evolution of the gas: (1) The longer the time of boiling the less the deviation from the supersaturation-velocity coefficient curve for water. This behavior is probably related to an irreversible hydrolytic change in which non-colloidal substances are formed. (2) The more rapid the cooling the greater the deviation from the water curve, probably because the reversible change sol-gel does not have time to go so far. This indicates that it is the sol which is responsible for the deviations. (3) The older the colloidal solution after boiling the less the deviation. This would promote the sol-gel change and bear out the above theory. (4) Through prolonged saturation the slope of the curve approaches that of water.

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Solubility and Size of Particles

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That precipitates which have been for some time in contact with the liquid, filter more readily than fresh precipitates, has long been a familiar observation. In analytical chemistry the necessity of digesting the precipitate with the liquid from which it was formed has long been recognized as a means of preventing the precipitate from passing through the filter. Curie[1] seems first to have pointed out that given a mixture of crystals of different sizes in contact with a saturated solution, the small crystals may go into solution and crystallization on the larger crystals may occur, so that the total surface, and therefore the surface energy between the solid and liquid decreases. This idea follows the relation between the larger and smaller drops of a liquid. Sulphur vapor may be condensed on a cold surface to a coating made up of exceedingly small drops of supercooled liquid. If maintained at constant temperature in time it will be noticed that some drops have become markedly larger, while in their vicinity many small drops have disappeared. This is not due to coalescence, but to a distillation from the smaller drops to the larger. The smaller drops with their greater curvature, have a greater vapor pressure than the larger drops. (Compare Gibbs' Scientific Papers, 1876.)

Sir William Thomson[2] showed the thermodynamic relationship between the vapor pressure of drops and their radii (curvature of the surface), arriving at the following equation:

$$\frac{RT}{M} \ln \frac{p_2}{p_1} = \frac{2\sigma}{\rho}\left(\frac{1}{r_2} - \frac{1}{r_1}\right)$$

where RT has the usual significance, M the molecular weight of the liquid, the surface energy and the density of the liquid, p_1 and p_2 the vapor pressures of the droplets of radii r_1 and r_2. The similarity between the evaporation of a liquid or a solid and of solution of a solid in a liquid solvent is so well established that the above ideas may be applied to solid particles in contact with their solution. This consequence was pointed out by Ostwald.[3] Experimentally Ostwald investigated the relationship between the red and yellow modifications of mercuric oxide, showing that the yellow modification shaken with a KBr solution liberated more KOH than did the red form and was therefore more soluble. The reaction is $HgO + KBr + H_2O \rightleftarrows 2KOH + HgBr_2$. Ostwald also obtained results with calcium oxalate which showed less solubility for the larger crystalline precipitate as compared with the same precipitate ground fine with garnets on the ball mill principle. He observed a difference of 0.9 per cent. Calcium iodate showed a 3 per cent difference in the solubility of the finely ground substance. The concentrations were measured volumetrically. Also $Ba(NO_3)_2$, $HgCl_2$ and $PbCl_2$ were examined by using a pycknometer to determine a change in concentration. He observed an increase in density of the solution saturated with the finely ground material. $Ba(NO_3)_2$ showed the least and lead chloride showed the greatest change. Ostwald also deduced the relation between the size of particles, solubility and surface tension. The relation developed by Ostwald was later corrected by Freundlich in his Kapillar-Chemie (1909, p. 144).

$$\frac{RT}{M}\, ln\, \frac{s_2}{s_1} = \frac{2\sigma}{\rho}\left(\frac{1}{r_2} - \frac{1}{r_1}\right)$$

RT and *M* have the usual significance, s_1 and s_2 are the concentrations of the solutions in equilibrium with particles of radii r_1 and r_2 respectively, σ the surface energy, ρ the density of the solid.

This equation is seen to be entirely similar to that developed for the vapor pressure of small drops of liquid. But in the case in hand the concentrations of the solutions s_1 and s_2, and their osmotic pressures, balance the solution pressure of the particles r_1 and r_2 at equilibrium, so that the similarity is quite complete. However, in the case of electrolytes, the factor of dissociation may be taken into account, as has been done by Jones.[4]

If the dissociation of the saturated solutions are different in amount the osmotic pressure and, therefore, the work in passing from one to the other, may be calculated by introducing into the Ostwald-Freundlich equation a factor which takes account of the difference, as Jones (*loc. cit.*) has done, who arrives at the following relation:

$$\frac{2\sigma}{\rho}\left(\frac{1}{r_2} - \frac{1}{r_1}\right) = \frac{RT}{M}\left[(n-1)(\gamma_1 - \gamma_2) - \frac{m}{m-1}\, ln\, \left(\frac{1-\gamma_1}{1-\gamma_2} + \frac{m}{m-1} \log \frac{\gamma_1}{\gamma_2}\right)\right]$$

γ is the degree of dissociation, n — is the number of ions from one molecule, m — is the constant from Stork's dilution formula.

Dundon and Mack,[5] in calculating the surface energy of calcium sulphate, have considered this relation and pointed out that if it be assumed that the dissociation is constant during the process one may write

$$(1 - \alpha + n\alpha)\, \frac{RT}{M}\, ln\, \frac{S_2}{S_1} = \frac{2\sigma}{\rho}\left(\frac{1}{r_2} - \frac{1}{r_1}\right)$$

and find that the calculated surface tension is practically the same as that calculated by the more rigorous equation of Jones. Furthermore, r_2 is the radius of the small particle measured by the microscope and r_1 that of a particle so large that the solubility is that of plane surface and may be put equal to infinity. And thus the equation becomes

$$1 - \alpha + n\alpha)\, \frac{RT}{M}\, ln\, \frac{S_r}{S} = \frac{2\sigma}{\rho r}$$

which may be used in calculating surface energies between solids and their saturated solutions, at least until more accurate data on size of particles are at hand.

Dundon[7] has carefully repeated and extended some previous work of Hulett[6] and found that finely divided gypsum added to a saturated solution of gypsum caused an increase in conductivity which rose to a maximum and then slowly decreased, finally approaching the normally saturated, clearly corresponding to changing solubility with changing size of particles. The size of particles were measured under the microscope and the solubility calculated from conductivities. From these data the surface tension was calculated and appeared to be about 370 dynes per square centimeter. Careful observations[7] were made on lead fluoride, lead iodide, barium sulphate, strontium sulphate and calcium fluoride. From the observations the following surface tensions have been calculated:

Substance	r_2	Per Cent Increase of Sol.	Calc.
PbI_2	0.4	2.0	130 dynes cm.
$CaSO_4.2H_2O$	0.2 to 0.5	4.4 to 12 per cent	370
Ag_2CrO_4	0.3	10.0	575
PbF_2	0.3	9.0	900
$SrSO_4$	0.25	26.0	1400
$BaSO_4$	0.1	80.0	1250 (Hulett)
$BaSO_4$	0.2	90.0	3000
CaF_2	0.3	18.0	2500

The difficulty of obtaining exact measurements of size of particles is the weak point in the calculated surface energies. The results with the above substances suggest a proportionality between surface energy and hardness and an inverse proportion between surface energy and molecular volume, as indicated by the Ostwald-Freundlich equation. A more precise determination of the dimensions of the particles would, no doubt, give a fairly reliable value for the surface energies of the substances in question.

W. C. M. Lewis[8] and Knapp[9] have considered the effect of an electrical charge on the surface tension and this may be a factor in the case of fine particles in contact with their solution.

W. D. Jones[10] has considered the influence due to various geometrical forms other than spheres. The method conductivity of determining the concentration of the solution is rapid and satisfactorily exact, and one may readily follow the changing concentrations. The work on gypsum indicates that the powder rapidly saturates a solution, but that the supersaturated solution is much slower to come to equilibrium in contact with the solid phase. This may be a factor in systems of various sized particles and solutions. The smaller particles, if present in considerable proportions would dominate the situation, and the real problem is to get a more exact idea of the size and relative numbers of the smaller particles when equilibrium is attained. Svedberg and Nicols[11] have devised a special form of centrifuge which permits of a photographic observation of the rate of precipitation of the dispersed phase under known conditions so that Stokes' law gives good values for the size of particles. This scheme might be applicable to the problem in hand.

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Attraction Intensity or Attraction Pressure

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In the year 1864 the apothecary, C. Musculus,[1] carried out a series of capillarity experiments by the capillary-rise method, on aqueous solutions of various substances, such as alcohol, acetic acid, albumen, soap, bile, different sugars and salts. He found that substances, such as alcohol, acetic acid, soap and bile had a marked effect in lowering the capillary rise of water, while other substances, such as the salts, etc., had but very little effect on this property. Musculus differentiated accordingly between capillary-active and capillary-inactive substances.

In a paper entitled "Capillary Phenomena in Relation to Constitution and Molecular Weight,"[2] J. Traube, taking his cue from the almost completely forgotten work of Musculus, made a systematic investigation of the surface tension of aqueous solutions of common substances[3] and from the collection of a large amount of numerical data he established the importance of classification into *surface-active* and *surface-inactive* substances.[4] He must therefore claim to have contributed in not an inconsiderable degree to the substantiation of this classification which is so important in capillary chemistry. It may also be stated that today this division is hardly less important than even the separation of substances into electrolytes and non-conductors. In the former as in the latter case there are no sharply differentiated groups but a gradual transition, which fact, however, does not detract from the usefulness of this classification.†

As is known, electrolytes are substances which are particularly distinguished as being *surface-inactive.* They generally increase the surface tension of water and the relationship between the surface tension of aqueous solutions and the concentration is represented by curves which are almost straight lines.

On the other hand, substances, such as the common alcohols, fatty acids, ethers, esters, etc., lower the surface tension of water to a greater or lesser extent; in this case the curves are parabolic. Such substances are called *surface-active.* In the case of substances of homologous series, the surface tension of water decreases the more strongly, the greater the number of the CH_2 groups; in dilute solution this decrease in the surface tension approaches the ratio 1 : 3. Accordingly, the decrease in the surface tension in homologous surface-active substances follows approximately the series $1:3:3^2$ - - - -.[5]

This rule has acquired great significance, particularly in biological fields, after it was shown[6] by the writer that the surface tension bore a very close causative connection with the processes of adsorption, osmosis, narcosis, etc. Especially in the lysis of cells (such as blood corpuscles), in the narcosis of tadpoles, in catalytic processes taking place in the presence of surface-active substances, in the protoplasmic current, in the destruction of cells, etc. All these show the approximate validity of this rule.[7]

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* Translated by Ismar Ginsberg, B.S., Chem. Eng.

† The author in giving here this short historical introduction, does so because, as far as he knows, credit has been given him in the literature in the field of surface tension, and particularly with respect to the introduction of the drop method. On the other hand nowhere is mention made of the fact that he proposed the first division of substances, on a strictly scientific basis, into surface-active and surface-inactive materials according to the laws of capillary chemistry.

The Gibbs-Thomson theorem is of especially great importance in understanding the mechanism of surface tension phenomena. In the first place this theorem explains the phenomena which take place at the interface between two phases, and accordingly bridges the gap between surface tension and adsorption phenomena.

Even in the work above referred to, the author referred to the relationships which must exist between *surface tension* and *solubility*. These relationships were later studied comprehensively by the author [8] and similarly the connection between surface tension and other entirely different properties of solutions.

In connection with solubility it was particularly shown that surface-active substances are displaced from their solutions by substances which increase the surface tension of water. This takes place more easily, in proportion as the displacing substance increases the surface tension of water and as the substance that is displaced lowers the surface tension of water. In a later paper [9] it was shown that the solubility of difficultly soluble salts is decreased by more or less surface-active organic compounds, the effect being greater in proportion to the surface-activity of the substance in question.

In a new contribution, not yet published, it has been established with reference to Neuberg's work, that certain organic salts, which *decrease* the surface tension of water (such as sodium salicylate, etc.), often raise, to a considerable extent, the solubility of surface-active compounds, such as amyl alcohol, etc.

All these and numerous other relationships, which have been developed by the writer and others, acquire what is sometimes a profound significance when attention is concentrated on a certain factor, which is none other than the magnitude of the attraction between the dissolved substance and the solvent, the well-known cohesion factor, a_{12}, developed by van der Waals—a factor which Traube terms *attraction pressure* or more correctly, perhaps, *attraction intensity*.

In order that a molecule of a substance dissolved in water may move from the interior of the liquid to the surface, a certain amount of work must be done. No material error is involved, if this work is set equal to the difference between the surface energies of water and of the solution. This difference corresponds to the surface activity and constitutes a measure of the attractive intensity, for the work in question consists in fact of nothing more than the energy involved in overcoming the forces of cohesion.

Accordingly the attraction intensity corresponds to the difference between the surface tensions of the solution and of water. The above-mentioned law for homologous surface-active substances states, accordingly, that the attraction intensities of surface-active homologous substances are related to each other like the terms of the series: $1 : 3 : 3^2$- - - - -. Substances of lower attraction intensities (greater surface activity) are displaced from solution by substances of greater attraction intensity (inorganic salts, etc.). The Gibbs-Thomson principle may be thus expressed: substances of lower attraction intensity concentrate in the interfaces between the phases and substances of higher attraction intensity leave the interfaces.

The well-known Hofmeister-Spiro ionic series is nothing more than the series of attraction intensities of the ions,[10] while anions, such as CNS, I, etc., are distinguished by their slight attraction intensities to water. On the other hand the reverse condition holds for the ions SO_4, CO_3, etc. Similarly the attraction intensity increases from Cs through K to Na and Li. The most diverse properties of ions, in particular their electro-chemical behavior, are very closely interrelated with the magnitude of the attraction intensity.[11]

Attraction intensity and *formation of submicrons* are very closely interrelated.[12] For example a one per cent aqueous solution of a salt of an alkaloid such as quinine hydrochloride has almost the same surface tension as water. The salt ions are dissolved in the state of a molecular dispersion. Their attraction intensity to water is considerable. When small quantities of alkali are added to such a solution, then numerous rapidly moving submicrons are observed.[13] The surface tension is strongly reduced and so correspondingly is the attraction intensity of the quinine particles. This decreased attraction intensity even leads to the formation of submicrons. It is therefore easy to understand that the forces of cohesion, which bring about the formation of submicrons, are the more effective the less the adhesion energy of the dissolved substance to the solvent.

It is possible to prepare solutions of nonylic acid having the same surface tensions as water.[14] The addition of a drop of a dilute solution of hydrochloric acid is then sufficient strongly to reduce the surface tension of the solution and coincident with the phenomenon the formation of numerous rapidly-moving submicrons is observed. Substances such as benzol, carbon tetrachloride, etc., which are difficultly soluble in water lower the surface tension to a scarcely perceptible degree. They are dissolved only to the submicronic stage. Substances which have a somewhat greater attraction intensity to water, such as octylic alcohol, caprylic acid, in the more concentrated state, are dissolved partly as submicrons and partly to molecular dispersion, and even in aqueous solutions of amyl alcohol and aniline numerous submicrons are still found in semi-saturated concentrations.[15] Furthermore, difficultly soluble salts such as AgCl, and $BaSO_4$ are dissolved as submicrons to at least a considerable extent. The magnitude of the attraction intensity dominates the distribution of the dissolved matter, determining whether it be molecularly dispersed, or in submicrons, or whether submicrons be formed from molecularly-dispersed particles. Substances which are only partially soluble in water, corresponding to their rather small attraction intensity, are dissolved more or less as submicrons. The aggregation of submicrons of surface-active substances at the interfaces, which was first observed by my pupil Klein [16] and was interpreted by the writer and Klein as a Gibbs phenomenon, may also be thus explained. The writer will discuss the importance of this much-discussed phenomenon in a later contribution

As far as the attraction intensity of *colloids* is concerned, we can speak of *hydrophobe* colloids, that is, colloids of slight attraction intensity. On the other hand there are the hydrophile colloids, such as albumen, gelatin, various gums, etc., which possess considerably greater attraction intensity. From this point of view we may understand the following: (1) that hydrophile colloids require much more electrolyte to throw them out than do hydrophobe colloids; (2) reversibility and irreversibility with reference to flocculation and re-solution; (3) especially the protective action for hydrophobe colloids of hydrophile colloids having a relatively high attraction pressure for water.

According to recent work by Traube and Rackwitz[17] colloids of greater attraction intensity, such as gelatin, albumen, etc., exert a powerful protective action on sols of gold, silver, etc., while on the other hand colloids possessing great surface activity and hence slight attraction intensity to water (such as soaps, saponin, salts of gallic acid, etc.) exert a very slight protective action. A simple explanation of the phenomena of sensitization is also afforded by this theory.

The field of *adsorption phenomena* becomes much clarified when we take into consideration the concept attraction intensity.

If an aqueous solution of a substance is in contact with a second phase, for instance, with a cell wall, then the chances for the adsorption of the dissolved substance by this second phase are apparently greater in proportion to the concentration of particles of the dissolved substance at the interface. Surface-active substances are therefore easily adsorbed and hence we must not be surprised to find that surface-active substances displace surface-inactive substances, such as the sugars, salts, etc., from the surface of solid adsorbents, such as carbon, etc. To be sure, the attraction intensity to water (the surface activity) determines only the degree of concentration in the neighborhood ot the interface. The actual adsorption, which is characterized by the cessation of the Brownian movement,[18] depends on a second attraction intensity, the attraction intensity to the absorbent. The less the attraction intensity to water and the greater the attraction intensity to the absorbent, the greater is the absorption. A characteristic phenomenon from this standpoint is the behavior of solutions of fatty acids towards different adsorbents, which was investigated by Traube and Nishizawa.[19] The lower fatty acids, such as formic, acetic, and propionic acid, have a relatively high attraction intensity to water. It is accordingly found that only a strong adsorbent, such as bone black, is able to adsorb large quantities of these acids; however the weaker adsorbents, such as barytes, or even zinc blende and lead glance cannot do so. In the case of valerianic acid it has been found possible to cause the adsorption of the acid in small proportions, under the concentration conditions which prevailed during the experiment, by such absorbents as barytes. On the other hand this was not possible in the case of zinc blende and lead glance. Capronic acid is adsorbed by the latter adsorbents, but not by a particularly poorly absorbent pyrite. On the other hand, caprylic acid, is spite of its very slight attraction intensity to water, is adsorbed to a greater or lesser degree by all the before-mentioned absorbents. The last two acids are easily and completely adsorbed by bone black.

A research, carried by Traube's pupil, R. Schulz,[20] on the distribution of a substance, dissolved in water, at the interface liquid-liquid, led to entirely analogous results, when the aqueous solution was brought into contact with a non-miscible organic solvent, such as benzol, etc. It was not possible to detect any distribution in the organic solvents under the chosen experimental conditions (see *loc. cit.*), when the attraction intensity of the dissolved substance towards water was relatively great. This was for example the case when a normal aqueous solution of ethyl alcohol or acetic acid was shaken with benzol in the presence of equal proportions of benzol and of aqueous solution. Neither ethyl alcohol nor acetic acid were detected in the benzol. On the other hand, if the attraction intensity was slight to water, but very great to benzol, as in the case of octyl alcohol or caprylic acid, then with the above proportions, right after a single shaking, the dissolved substance was no longer detectable in water, while for the moderately heavy fatty acids and alcohols a certain amount of distribution took place in accordance with their attraction intensity. Other results are described in the article referred to.

The lipoids play an important rôle in biology.

The theory of Ernst Overton is well known. In accordance with this theory the degree of distribution between the lipoid and water is determinative for the absorption of the dissolved substance by the cell surface and cell interior. In fact it may be stated that a reciprocal relationship exists between the attraction intensity of the substance to water and that to the organic solvent, especially in the case of lipoids. Therefore, it comes to pass that the surface activity, and therefore the attraction intensity to water, is the *main* criterion for the adsorption or the absorption of the substances by or in the lipoids, and that the lipoid theory suits the observed phenomena to a certain degree. On the other hand Traube's surface activity theory of adsorption and osmosis is a more general theory.

There is quite a marked parallelism between the surface activity of the substances dissolved in water and their *capacity* for being absorbed, as well as the speed of absorptivity by the cell.[21] It has thus been demonstrated by the author that the tendency of plant cells to plasmolysis generally parallels the surface activity of the dissolved substance. There is scarcely any deviation from this rule in the whole series of substances. The same relationship was manifested in the case of hemolysis of blood corpuscles in the swelling of muscle and many other similar phenomena,[22] so that there was an almost complete analogy between permeability phenomena and the magnitude of surface tension. These relationships became still more remarkable when they were substantiated by quantitative figures. It moreover was also indicated that the above-mentioned rule, which applies to the change in surface activity of homologous substances, is found to apply as well to the most variable permeability phenomena.[23] According to the investigations made by Fühner and Neubauer (see *loc. cit.*) it was shown that homologous substances have a like hemolyzing effect, when the concentration is allowed to increase with increasing number of CH_2 groups in the ratio $1:3:3^2$- - - - -, in fact to even a greater degree. According to the investigations made by Czapek and his disciples,[24] it was indicated that certain swelling values of the concentration of aqueous solutions of surface-active substances, which corresponded to the *iso-capillarity* of the solutions in question, were determinative for the destruction of plant cells, for example, the destruction of the germinative power of yeast.

And for all that, the meaning of these experiments is not so simple as at first appeared. All such adsorption and permeability experiments had taken place in plant or animal structures, that is, under indefinite conditions; that is, there were involved not exclusively aqueous protoplasmic structures, but also more or less lipoids.

Comparative experiments on adsorption and osmosis with aqueous solutions of surface-active substances, comparing, for example, an aqueous gelatin gel with another aqueous gelatin gel which contained increasing quantities of finely emulsified lecithin[25] led to the conclusion that it was possible easily to reproduce the same simple parallelism in relation between surface activity and both adsorption and osmosis, which are found in plant and animal preparations, only when lecithin is added to the gelatin gel or when more or less egg yolk is added to a gel of egg albumen. However, in the case of pure gelatin gels or albumen gels the known relationships referred to are only incompletely shown. In the latter case there was particularly no parallelism between surface activity and osmotic processes in the gel. Consequently the lipoids play a greater rôle in the osmotic phenomena in the organism than has often been thought, and the lipoid theory is not to be dismissed, although the Gibbs-Thomson theory and the surface activity theory of adsorption and osmosis, founded on it, are to be given first consideration.

We must not neglect in this connection to point out the deficiencies of the van't Hoff and Arrhenius solution theory. Biologists complain that they cannot begin to use this theory, as far as osmotic problems are concerned. Physical chemists further state that in all the attempts to corroborate this theory it fails on meeting the phenomena of solubility, surface tension, compressibility

This is only to be expected. When a certain amount of a substance is dissolved in a solvent, for example, water, then the water is converted into a solution. If the substance is uniformly distributed, then the energy, which is expended in the process of solution, is proportional to the number of particles, which are dissolved, and in addition to the attraction which the dissolving particles have for the water.

Only the capacity factors in the former case play any part in the van't Hoff and Arrhenius theories. The number of particles is the sole factor controlling the osmotic pressure. However the latter factor, which corresponds to the potential of the attraction intensity, is not found in the van't Hoff and Arrhenius equations. It is *just this factor* which is of prime importance, as we have seen, in the solubility phenomena of surface tension, adsorption, and also of volumetric relationships.[26]

Theories which do not take into consideration the attraction intensity are to be sure useful to a certain degree, but they are narrowly limited and therefore in no way comprehensive. An energy factor, for example, the electric energy EI, can be increased to the same extent by changing the value of E as well as that of I. However, when we take into consideration just one factor, as in the Arrhenius theory, then we are constrained in explaining the many variations, to assign all to the variability of that one factor, the number of particles, and even where another factor, the attraction intensity, may play a part.

This brief review may suffice to justify the reserve with which the author, in contradistinction to many scientists, has received modern solution theories. The author unquestionably recognizes the good points inherent in these theories—particularly the thermodynamics of van't Hoff; but he deplores the fact that many scientists of the older generation should exhibit intolerance toward those investigators (himself unquestionably among them), who do not regard these theories as dogmas beyond criticism.

In the meanwhile, however, science has busied itself with other questions, even though the unsolved problem regarding theories of solution continues to prevent an accurate conception of solution. Just as the classic gas law found its supplement in van der Waal's equilibrium equation, so too in the laws of solution an equation must be found which gives proper consideration to *attraction intensity.*

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Quantitative Investigations on the Changes in Strength of Union with Water Exhibited by Hydrates with Crystallization Water when their Degree of Dispersity Is Changed by Mechanical Means

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I. Preface

That the physical properties of substances are functions of the size of the particles these substances are constituted of, is an acquisition dating back to the work of Lord Kelvin, J. Goldstein, Wilhelm Ostwald, G. A. Hulett, C. Doelter, P. P. von Weimarn, W. Kuester, P. Pawlow and others. This dependence has been established both theoretically, as well as on experimental grounds, for such properties as, *e.g.*, solubility, vapor tension, boiling and melting points.[1]

This rule, however, is not confined in its application to physical properties alone, but it holds good for the chemical properties as well.

A quantitative investigation would be of considerable interest of the changes undergone by hydrates with crystallization water with respect to the strength of union with water, consequent on the change in degree of dispersity of these hydrates brought about by mechanical means.

The present paper is to deal with the results of such an investigation carried out with two representatives of hydrates with crystallization water: the $Al_2O_3 . 3H_2O$ and the $Fe_2O_3 . H_2O$. The water is known to be retained by the crystals of these substances with such a strength that it has even been described as water of constitution.

In 1907 a theory was advanced by P. P. von Weimarn [2] according to which the strength of union with the hydrate water would diminish in the hydrate-crystals (*e.g.*, those of $Al_2O_3 . 3H_2O$) as the degree of dispersity of the crystals is increased (viz.: as the grain size is reduced), so that at a certain very high degree of dispersity the hydrate water may no longer be distinguished from the so-called adsorption water.

In one of his papers on the problem, P. P. von Weimarn [3] made the following statement:

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* A more detailed presentation of that work, especially from its theoretical side, see: P. P. von Weimarn and T. Hagiwara, "Static and Dynamic Solvations in Connection with the Dispersity Degree of the Substance" (now in state of preparation for the "Kolloidchem. Beih.").

About the results of x-ray investigations (by the Debye-Scherrer-Hull method) of highly-disperse powders prepared by mechanical grinding of crystal-hydrates of the hydroxides of aluminium and iron, see: P. P. von Weimarn and T. Hagiwara, "Amorphy Doctrine is Delusion," *Koll.-Zeitschr.* 1925.

> "Just as an ordinary skeleton-frame may collapse if a few beams are missing or caused to break, unless fresh building materials are duly supplied and other beams are substituted for the broken or the missing ones, so may an $Al_2O_3.3H_2O$ crystal of a size inferior to that of its standard frame, lose its water at a lower temperature, and become *anhydrous* even if no influx of fresh foodstuff from the solution is provided for, taking place at a suitable rate";

and further, in another paper:[4]

> "Finally, with extremely fine-disperse crystalline precipitates (gelatinous), the binding of water will be reduced in strength to such an extent that the hydrate water will be scarcely distinguishable from the water as present in a wetted common bath sponge."

In regard to aluminium hydroxide as precipitated by chemical reactions in an aqueous medium, it was stated by P. P. von Weimarn in one of his books[5] that the higher the degree of dispersity of the precipitate, the lower will be the temperature at which the precipitate would begin to give off its water.

A few words would not be amiss concerning prior work devoted to the dehydration process in amorphous and colloidal (gelatinous) hydrates. W. Ramsay,[6] later T. Carnelley and J. Walker,[7] have studied the dehydration rate at varying temperatures for the so-called "amorphous" ammonia-precipitated hydroxides of aluminium, iron and other metals. From this study they arrived at the conclusion that, in the amorphous state, either no definite hydrates existed at all, or there were very many of them, showing but very slight divergence in vapor tension, so that the smallest rise or fall of temperature would suffice to convert a higher into a lower hydrate or vice versa.

In one of his most remarkable papers (1888) J. M. van Bemmelen[8] was able to show that the dehydration curves (see diagrams below) offered by the so-called colloid (gelatinous) hydrates would display essential divergence in type from similar curves for the same substances when in the form of crystalline hydrates, the dehydration curves corresponding to the hydrates-colloids being quite smooth, while sharp breaks would be shown by the same curves plotted for the hydrates-crystals.

We thus come to see that much stress has been laid in the older researches on the difference in behavior exhibited with respect to dehydration by the amorphous and the colloid hydrates on the one hand and the same hydrates when in a crystalline condition on the other.

P. P. von Weimarn, on the other hand, has worked out a theory,[9] according to which, by way of disintegrating crystals of any substance, the material of these crystals may be prepared in a colloid condition. This assertion of P. P. von Weimarn's was of course meant to comprise such crystals as well as those of $Al_2O_3 . 3H_2O$, of $Fe_2O_3 . H_2O$ and the like.

And in point of fact, A. L. Stein,[10] availing himself of P. P. von Weimarn's method, was able to prepare colloid solutions of aluminium and iron hydroxides, starting from beautiful natural crystals of diaspore ($Al_2O_3 . H_2O$) and iron glance (Fe_2O_3), and using lactose as inert substance to help subdivision. A colloid solution of aluminium hydroxide has later (1922) been prepared by the same method by S. Utzino[11] (the particle size reached was about 59.8 μμ) from artificially formed microcrystals of $Al_2O_3 . 3H_2O$, with glucose as inert matter.

These experiments prove beyond the possibility of any reasonable doubt that mechanical subdivision of crystals may actually bring forth their conversion into the state of colloid solutions.

If now evidence is to be adduced of the fact that by mechanical subdivision of crystals like those of $Al_2O_3 . 3H_2O$ and $Fe_2O_3 . H_2O$, the water of constitution contained therein is being converted into colloidally-bound water, it is of course necessary to realize the dehydration curves for these crystals for different degrees of dispersity.

II. EXPERIMENTAL

1. Experiments with $Al_2O_3 . 3H_2O$.

The experiments have been carried out with microcrystalline aluminium hydroxide prepared by Bonnsdorff's method, viz., by extremely slow precipitation from alkaline saturated aluminium hydroxide solutions. The precipitate obtained was made up of white granular particles which, when examined under the microscope, proved to be characteristic needle-like crystals. After thorough washing, the precipitate was kept in a desiccator over concentrated sulphuric acid for two weeks, until constant weight was reached by the sample. The results of analysis were as follows:

Per cent water in $Al_2O_3.3H_2O$, theoretically	34.59
Per cent water in $Al_2O_3.3H_2O$ microcrystals, analytically determined...	34.59
Difference	0.00

Hence: $x = 3.00$.

In order to obtain a finely-divided sample, the above microcrystals were pulverized with fine quartz powder in an agate mortar, the procedure being as follows: 0.1 gram of the microcrystals were mixed with 0.4 grams of quartz powder and ground for one hour by hand; this operation being repeated four additional times, the five portions (each portion containing 0.1 gram $Al_2O_3 . 3H_2O$ and 0.4 grams quartz) of ground matter, were then added together and ground for half an hour again. The mixture thus obtained was subsequently kept in a desiccator over concentrated sulphuric acid for two months, which proved enough for the substance to reach a perfectly constant weight. The total water content of the sample was then determined by ignition; under the assumption that the whole amount of water would pertain to the Al_2O_3, the results obtained from analysis were:

Per cent water in $Al_2O_3.3H_2O$, theoretically	34.59
Per cent water in the $Al_2O_3.3H_2O$ ground with quartz, as determined analytically	37.30
Difference	2.71

Hence: $x = 3.235$.

The samples thus prepared were then submitted to dehydration in an electric oven (permitting to maintain a constant temperature within ± 1°) at temperatures ranging between 90° and 220° Centigrade. Previous to the determination, after each heating, of the water content of the samples, these were always allowed to arrive at a practically constant weight, by keeping them in a desiccator containing concentrated sulphuric acid.

The results obtained are shown in Tables I and II. The dehydration curves in Fig. 1 were obtained by plotting the water content in mols remaining in the samples along the axis of ordinates against temperatures as abscissæ, so that each point in the curves indicated the amount of water contained in the samples when heated to practically constant weight at the corresponding temperature.

TABLE I*

MICROCRYSTALS $Al_2O_3.3H_2O$ (PREPARED BY BONNSDORFF'S METHOD)

See Fig. 1, curve A.

Temperature in ° C.	Duration of Heating, Hours	Composition in Mol.
100	0.5	3.00
120	0.5	3.00
149	0.5	2.96
160	1.0	2.94
165	0.5	2.93
170	5.5	2.84
180	5.0	2.82
190	5.0	2.79
200	8.0	2.65
210	20.0	1.14
220	8.0	0.89

TABLE II*

$Al_2O_3.3H_2O$ MICROCRYSTALS GROUND WITH QUARTZ

See Fig. 1, curve B.

Temperature in ° C.	Duration of Heating, Hours	Composition in Mol.
Room temperature	—	3.24
90	2.0	2.87
100	8.0	2.76
110	5.0	2.63
120	5.0	2.45
130	25.0	2.12
140	11.0	2.01
150	14.0	1.73
160	16.5	1.41
180	24.0	0.71

* T. Hagiwara, *Koll.-Zeitschr.*, 32, 154 (1923).

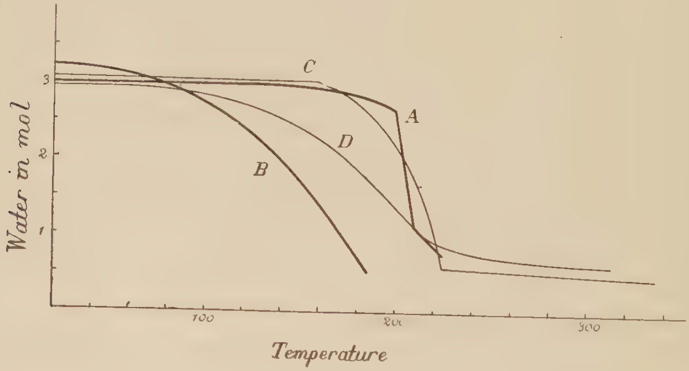

FIG. 1.

Seeing that absolute equilibrium may not be reached so soon at every temperature—which is true especially of finely-divided materials—the heating was actually carried on until approximately constant weight was reached. The rate of this dehydration is to be dealt with later on, in connection with the case of the iron compound.

That but very small quantities of water are adsorbed by finely-ground quartz, may clearly be seen from Table III. We may therefore consider as very insignificant the effect of quartz in the way of augmenting the amount of water adsorbed by the ground mixtures of quartz and hydroxide.

The dehydration curve A in Fig. 1 is the one obtained by the author for microcrystals of $Al_2O_3 . 3H_2O$, and the dehydration curve B is that found by the author for the powder of the same $Al_2O_3 . 3H_2O$ ground with quartz.*

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* It should be borne in mind that the dehydration curves *B* and *C* thus obtained represent, as it were, resultants of the various curves corresponding to the different sizes of grain making part of the powder under investigation, since these powders are "polvdisperse."

TABLE III *

Pure Quartz Powder Ground During 330 Minutes

Temperature in ° C.	Duration of Heating, Hours	Weight in Gr.
Room temperature	—	1.9717
100	1.5	1.9712
120	1.5	1.9709
120	5.0	1.9709
130	8.0	1.9707
140	6.0	1.9707
150	6.0	1.9707
160	6.0	1.9702
180	3.0	1.9702
180	7.0	1.9702

* The quartz powder was kept over concentrated sulphuric acid in a desiccator during two weeks.

If we compare with each other the curves A and B, we shall obtain conclusive evidence that not only does the increase in degree of dispersity (decrease in particle size) of the hydrate with crystallization water: $Al_2O_3 . 3H_2O$ cause the dehydration curve to become smooth (to exhibit no sharp breaks), but that it also compells the water to be set free at temperatures considerably lower than those at which it is set free from coarsely dispersed hydrates with crystallization water.

The diagram in Fig. 1 is sufficiently eloquent, indicating that, on reaching colloidal degrees of dispersity—whether this be done by chemical (curve D) or mechanical (curve B) means—the union of water in the hydrates with crystallization water becomes weakened to such an extent that it may be characterized as "adsorption" water.

For the sake of comparison, in addition to his own dehydration curves A and B, two more curves—C and D—were plotted by the author, in Fig. 1, corresponding to the experimental results obtained by J. M. van Bemmelen; of these curves the curve C relates to a microcrystalline precipitate similar to the one prepared by the author; the curve D is that of a hydrogel prepared by precipitation with ammonia and kept for one year in contact with water, and whose composition: $(Al_2O_3)2.9H_2O$ has suffered no alterations for six months when kept in a dry medium.

We need but to look at all these curves (see Fig. 1) to satisfy ourselves that there is agreement in type of the curve for the pulverized hydroxide (curve B) and the curve for the hydrogel (curve D).

2. Experiments with $Fe_2O_3 . H_2O$.

The iron hydroxides used were beautiful natural crystals of goethite ($Fe_2O_3 . H_2O$). Before the beginning of the experiments the crystals were kept for a week over concentrated sulphuric acid. The analysis gave the following results:

Per cent water in $Fe_2O_3.H_2O$, theoretically	10.138
Per cent water in $Fe_2O_3.H_2O$ natural crystals, analytically determined	10.151
Difference	00.013
Per cent Fe_3O_3 in $Fe_2O_3.H_2O$, theoretically	89.862
Per cent Fe_2O_3 in $Fe_2O_3.H_2O$ natural crystals, analytically determined	89.550
Difference	00.310

Hence: $x = 1.005$.

In order to prepare finely-pulverized material, the grains of the natural crystals were ground, as in the previous experiment, with fine quartz powder in an agate mortar. In the present series of experiments two samples of different fineness have been prepared by grinding; we shall describe them as "grinding A" and "grinding B," the mode of preparation being as follows:

"Grinding A": 0.2 grams of goethite and 0.8 grams of quartz powder were placed in an agate mortar and ground for two hours by hand. All in all there were five portions prepared as described above, which were finally all added together and ground for one hour more. The mixture was then left for 40 days in a desiccator containing concentrated sulphuric acid, until it showed perfect constancy of weight. The total amount of water was assumed pertaining to Fe_2O_3 alone, and on this assumption the analysis gave a water content corresponding to the formula: $Fe_2O_3 . 1{,}12H_2O$.

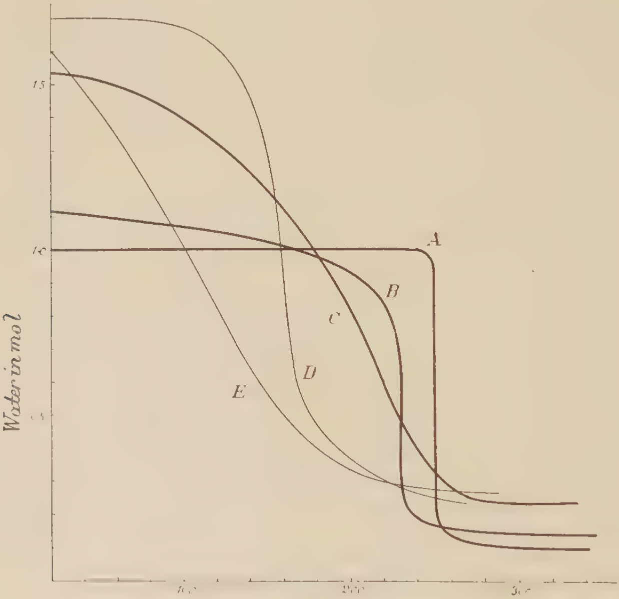

FIG. 2.

"Grinding B": The procedure in grinding was as follows: the first operation was preparing a mixture of 1 gram goethite and 4 grams quartz powder; this mixture was then divided into five portions: 1a, 1b, 1c, 1d and 1e and ground for 10 hours each; the second operation consisted in adding, to each of the above portions 0.2 grams quartz powder, and grinding the mixtures thus obtained for 5 hours each; the third operation was adding to the five portions: 2a, 2b, 2c, 2d and 2e, 0.2 grams quartz powder each, and grinding them for 5 hours again; the five portions: 3a, 3b, 3c, 3d and 3e thus obtained were finally mixed together, to form "grinding B."

The material obtained as a result of this grinding was then placed in a desiccator containing concentrated sulphuric acid and so kept for 50 days, until the weight of the powder became approximately constant. On the assumption that the total amount of water determined in the mixture would belong to the Fe_2O_3 alone, the composition of the mixture was found to agree with the formula: $Fe_2O_3.1{,}534H_2O$. As in the case of $Al_2O_3.3H_2O$, the dehydration was carried out in an electric oven, the procedure on experimenting being also the same.

In Tables IV, V and VI the results are drawn up for "natural goethite," "grinding A" and "grinding B" respectively, and the corresponding curves are plotted in Fig. 2 as A (natural goethite), B (grinding A) and C (grinding B).

TABLE IV

Natural Crystal $Fe_2O_3.H_2O$ (Göthite)

See Fig. 2, curve A.

Temperature in ° C.	Duration of Heating, Hours	Composition in Mol.	Rate of Dehydration per Hour	
Room temperature	—	1.005 H_2O	—	
90	5.0	const.	—	
130	5.0	"	—	
160	5.0	"	—	
190	5.0	"	—	
220	4.0	"	—	
240	5.0	"	—	
250	5.0	0.992 H_2O	0.0026 H_2O	
250	5.0	0.984 "	0.0017 "	Mean velocity
250	5.0	0.973 "	0.0024 "	
250	8.5	0.944 "	0.0034 "	
250	6.5	0.917 "	0.0042 "	
250	5.0	0.896 "	0.0042 "	0.0035 H_2O
250	5.0	0.874 "	0.0044 "	
250	7.5	0.842 "	0.0043 "	
250	7.5	0.809 "	0.0043 "	
250	10.0	0.766 "	0.0043 "	
265	2.0	0.735 "	0.0158 "	
265	1.0	0.711 "	0.0237 "	
265	1.0	0.687 "	0.0239 "	
265	2.0	0.656 "	0.0157 "	
265	2.0	0.614 "	0.0205 "	
265	2.0	0.564 "	0.0250 "	
265	1.0	0.543 "	0.0216 "	
265	1.0	0.525 "	0.0174 "	
265	1.0	0.509 "	0.0161 "	
265	1.0	0.484 "	0.0250 "	
265	1.0	0.466 "	0.0184 "	0.0107 H_2O
265	5.0	0.379 "	0.0173 "	
265	5.0	0.324 "	0.0110 "	
265	5.0	0.259 "	0.0130 "	
265	10.0	0.191 "	0.0068 "	
265	5.0	0.174 "	0.0034 "	
265	4.0	0.169 "	0.0013 "	
265	5.0	0.158 "	0.0021 "	
265	5.0	0.144 "	0.0028 "	
265	5.0	0.137 "	0.0015 "	
265	5.0	0.135 "	0.0002 "	
290	5.0	0.113 "	0.0045 "	
290	5.0	0.109 "	0.0007 "	
290	5.0	const.	—	
320	5.0	0.102 "	0.0015 "	
320	5.0	const.	—	

TABLE V

CRYSTAL HYDRATE $Fe_2O_3 . H_2O$ GROUND WITH QUARTZ

See Fig. 2, curve B.

"Ground A."

Temperature in ° C.	Duration of Heating, Hours	Composition in Mol.	Rate of Dehydration per Hour
Room temperature	—	1.121 H_2O	—
70	5.0	1.105 “	0.0032 H_2O
70	5.0	1.095 “	0.0020 “
70	5.0	1.098 “	—
90	3.0	1.082 “	0.0043 “
90	3.0	1.076 “	0.0020 “
90	3.0	1.075 “	0.0003 “
110	3.0	1.066 “	0.0030 “
110	3.0	1.061 “	0.0020 “
110	3.0	1.061 “	0.0000 “
130	3.0	1.051 “	0.0033 “
130	3.0	1.045 “	0.0020 “
130	3.0	1.046 “	0.0013 “
150	3.0	1.036 “	0.0033 “
150	3.0	1.029 “	0.0023 “
150	3.0	1.031 “	—
170	3.0	1.022 “	0.0030 “
170	3.0	1.009 “	0.0040 “
170	3.0	1.004 “	0.0017 “
170	3.0	1.001 “	0.0010 “
170	4.0	0.999 “	0.0005 “
190	3.0	0.984 “	0.0050 “
190	3.0	0.972 “	0.0039 “
190	4.0	0.959 “	0.0032 “
190	5.0	0.953 “	0.0012 “
190	3.0	0.952 “	0.0005 “
210	5.0	0.924 “	0.0056 “
210	5.0	0.908 “	0.0031 “
210	5.0	0.903 “	0.0001 “
210	5.0	0.895 “	0.0017 “
230	5.0	0.856 “	0.0078 “
230	5.0	0.830 “	0.0051 “
230	5.0	0.798 “	0.0065 “
230	5.0	0.762 “	0.0071 “
230	5.0	0.742 “	0.0042 “
230	5.0	0.710 “	0.0063 “
230	5.0	0.678 “	0.0065 “
230	5.0	0.651 “	0.0054 “
230	10.0	0.598 “	0.0053 “
230	10.0	0.555 “	0.0042 “
230	5.0	0.536 “	0.0039 “
230	10.0	0.509 “	0.0027 “
230	8.0	0.476 “	0.0041 “
230	7.0	0.440 “	0.0052 “
230	10.0	0.415 “	0.0025 “
230	10.0	0.390 “	0.0026 “
230	10.0	0.386 “	0.0004 “
230	5.0	0.368 “	0.0035 “
230	5.0	0.357 “	0.0021 “
230	10.0	0.347 “	0.0010 “
230	2.5	0.348 “	—
250	4.0	0.297 “	0.0125 “
250	11.0	0.224 “	0.0066 “
250	10.0	0.198 “	0.0026 “

TABLE V—*Continued*

Temperature in ° C.	Duration of Heating, Hours	Composition in Mol.	Rate of Dehydration per Hour
250	5.0	0.192 H_2O	0.0012 H_2O
250	5.0	0.173 “	0.0039 “
250	5.0	0.175 “	—
280	5.0	0.164 “	0.0018 “
280	10.0	0.154 “	0.0010 “
280	5.0	0.151 “	0.0006 “
280	5.0	0.149 “	0.0004 “
280	5.0	0.149 “	0.0000 “
320	5.0	0.144 “	0.0009 “
320	5.0	const.	—

TABLE VI

CRYSTAL HYDRATE $Fe_2O_3.H_2O$ GROUND WITH QUARTZ

See Fig. 2, curve C.

“Ground B.”

Temperature in ° C.	Duration of Heating, Hours	Composition in Mol.	Rate of Dehydration per Hour
Room temperature	—	1.534 H_2O	—
90	5.0	1.495 “	0.0078 H_2O
90	10.0	1.465 “	0.0030 “
90	5.0	1.447 “	0.0036 “
90	10.0	1.437 “	0.0010 “
120	5.0	1.359 “	0.0156 “
120	10.0	1.328 “	0.0031 “
120	5.0	1.320 “	0.0008 “
150	5.0	1.246 “	0.0148 “
150	15.0	1.187 “	0.0039 “
150	8.0	1.181 “	0.0007 “
170	5.0	1.152 “	0.0058 “
170	5.0	1.133 “	0.0038 “
170	10.0	1.116 “	0.0017 “
170	10.0	1.088 “	0.0028 “
170	5.0	1.053 “	0.0070 “
170	5.0	1.055 “	—
190	5.0	1.075 “	—
190	5.0	1.031 “	0.0024 “
190	10.0	1.008 “	0.0023 “
190	10.0	0.975 “	0.0033 “
190	10.0	0.965 “	0.0020 “
190	4.0	0.973 “	—
190	6.0	0.912 “	0.0053 “
210	5.0	0.859 “	0.0106 “
210	10.0	0.806 “	0.0053 “
210	8.0	0.779 “	0.0034 “
210	10.0	0.757 “	0.0022 “
210	10.0	0.745 “	0.0012 “
210	7.0	0.738 “	0.0011 “
210	10.0	0.742 “	—
210	10.0	0.726 “	0.0006 “
210	5.0	0.710 “	0.0031 “
230	5.0	0.681 “	0.0059 “
230	10.0	0.612 “	0.0069 “
230	10.0	0.577 “	0.0035 “
230	4.0	0.553 “	0.0059 “
230	5.0	0.539 “	0.0027 “
230	10.0	0.532 “	0.0008 “

TABLE VI—*Continued*

Temperature in ° C.	Duration of Heating, Hours	Composition in Mol.	Rate of Dehydration per Hour
230	10.0	0.520 H_2O	0.0012 H_2O
230	10.0	0.500 "	0.0019 "
230	5.0	0.500 "	0.0000 "
270	5.0	0.326 "	0.0349 "
270	5.0	0.310 "	0.0031 "
270	10.0	0.290 "	0.0020 "
270	10.0	0.292 "	—
270	10.0	0.271 "	0.0010 "
270	10.0	0.257 "	0.0014 "
310	5.0	0.237 "	0.0039 "
310	10.0	0.232 "	0.0006 "
310	5.0	0.241 "	—
310	10.0	0.253 "	—

In agreement with what was expected to occur, the dehydration of the natural goethite crystals (curve A) began just above 240° C.; while at temperatures below 240° the composition of the substance remained perfectly constant, being that of the monohydrate, at this point a sharp break occurs.

If now we turn our attention to the curve B * for "grinding A," we realize that the temperature at which loss of water begins appears displaced to the left side, towards lower temperatures, and that the well-pronounced break observed in curve A underwent transformation into a sensibly smooth bend.

And the dehydration curve C * which corresponds to "grinding B," *i.e.*, to a powder of still higher degree of dispersity than that of the "grinding A," fails already to exhibit any traces whatever of the sharp break characteristic of the dehydration curve A which corresponds to coarsely dispersed crystals; the curve C shows rather complete agreement in type with the dehydration curves as obtained for colloidal (gelatinous) hydrates prepared by chemical precipitation.

The most conclusive evidence of the correctness of our reasoning is afforded by the dehydration curves plotted by the author in Fig. 2 according to J. M. van Bemmelen's data for the so-called "yellow" and "reddish-brown" colloid precipitates of iron hydroxide.

We need but compare the form of the curve D for the "yellow" colloid iron hydroxide precipitate with that of the author's curve B for "grinding A," to see clearly that they are almost identical; for if we lift the curve B and displace it somewhat to the left, it may be brought sensibly to coincide with curve D.

As regards the curve E for the "reddish-brown" colloid iron hydroxide precipitate, its lower part is altogether identical in type with the curve C for "grinding B."

There are two conclusions to be derived from this comparison: firstly, that the "yellow" colloid iron hydroxide precipitate is of a lower degree of dispersity (contains larger particles) than is the "reddish-brown" one; and secondly, that a dehydration curve closely approaching the curve E may be obtained for the goethite by more perfect subdivision than that of "grinding B."

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* It should be borne in mind that the dehydration curves *B* and *C* thus obtained represent, as it were, resultants of the various curves corresponding to the different sizes of grain making part of the powder under investigation, since these powders are "polydisperse."

A further point of interest to be raised in the present connection is the agreement in type of the dehydration curves for the mineral limonite studied by H. W. Fischer[12] with the curve for "grinding A" found by the author (see Fig. 3; the broad line is that of "grinding A").

As regards the dehydration rate in the cases studied by the author, it was found to show successive rise as the temperature rose, from 240° C.—the temperature at which the hydrate starts setting free its water—up to 265° C. (see Table IV); the last 0.1 mol of water is, however, never driven off even at 320° C.

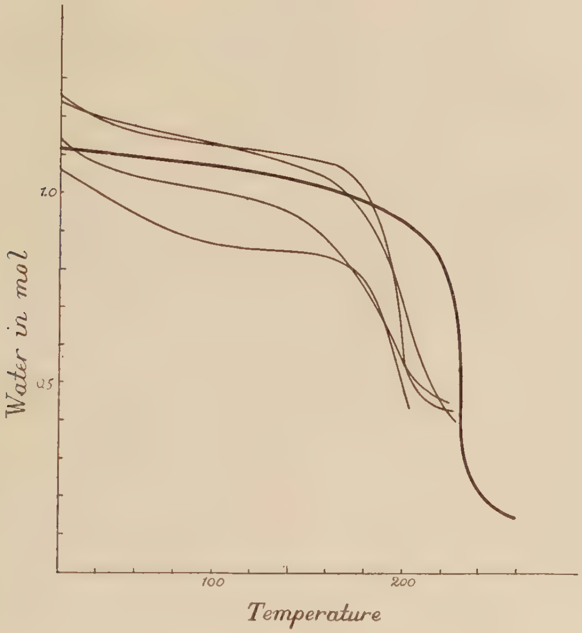

FIG. 3.

III. CONCLUSIONS

On the ground of his experimental results, the author feels himself entitled to draw the following general conclusion: by means of progressive mechanical subdivision of crystals of hydrates with crystallization water, viz.: by increasing the degree of dispersity of these crystals, a change in form of the dehydration curves is obtained, which may be carried so far that the curves would assume a form hitherto believed to be characteristic of the dehydration curves of the so-called colloid (gelatinous) hydroxides.

To put it in a different way, the progressive increase in degree of dispersity brought about by mechanical disintegration of a crystalline substance leads to the transformation of "crystallization" into, as it were, "adsorption" water.

All the above experimental results show perfect agreement with the requirements of P. P. von Weimarn's theory.

The present experiments were carried out in the Laboratory of Physical Chemistry of the Kyoto Imperial University; the author's thanks are due to the Director of the said laboratory, Prof. Y. Osaka.

Acknowledging his indebtedness to Prof. P. P. von Weimarn for the suggestion of the problem treated, the author wishes to express his thanks to Prof. P. P. von Weimarn for having guided the author's work.

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Quantitative Researches on Mechanical Dispersoid Synthesis

Under direction of Prof. Dr. P. P. von Weimarn *

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INTRODUCTION

The preparation of disperse systems by means of purely mechanical disintegration of crystalline substances has so far received but little exact quantitative study. In 1910 a mechanical method was suggested by P. P. von Weimarn,[1] consisting in the progressive grinding of the substance together with some other indifferent solid dilution material.† The dilution material is to be selected so as to dissolve easily in the liquid dispersion medium, while leaving the particles of the pulverized substance in the colloidal state.

On the basis of his crystallization theory of the colloids P. P. von Weimarn was led to suggest the preparation of colloids by grinding crystals; the very idea would obviously seem preposterous, to convert crystals into colloids simply by mechanical treatment, so long as "colloid" and "crystal" were regarded as antithetic concepts.

According to P. P. von Weimarn's theory of mechanical disintegration, it is possible to prepare a series of disperse systems of progressively increasing degree of dispersity, by progressively grinding a crystalline substance with increasing amounts of dilution material.

In his work, "Kolloides und kristalloides Loesen und Niederschlagen" (Kyoto, 1921),[2] P. P. von Weimarn has further recommended the application of low temperatures, *e.g.*, of liquid air and of a mixture of solid carbon dioxide and ether. According to his opinion, the grinding at very low temperatures would stimulate the action on each other of the atoms of the substance and the dilution material, thus favoring dispersoid synthesis.

The first to apply the above P. P. von Weimarn's theory of mechanical division for practical purposes was N. Pihlblad,[3] who thus succeeded in preparing a hydrosol of "Anilinblue 2B" by grinding it with the addition of urea.

Afterwards he ground rhombic sulphur[4] with urea in an agate mortar; he proceeded as follows: first 0.0522 g. S + 0.4698 g. urea ground for half an hour; then 0.1214 g. of this mixture + 1.0929 g. urea ground for 40 minutes, and last 0.1180 g. of this second mixture + 1.0620 g. urea ground 40 minutes.

By placing the powders thus prepared in water, he obtained a series of sulphur hydrosols; in these he determined the size of particles as follows:

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* For a more detailed presentation of that work, especially from its theoretical side, see: P. P. von Weimarn and S. Utzino: "Mechanical Dispersoid Synthesis, its Theory, and the Results Obtained in Practice" (now in state of preparation for the "Kolloidchem. Beih.").

About the influence of electrolytes on the dispersoid solutions prepared by the mechanical method, see: P. P. von Weimarn and S. Utzino, *Memoirs of the College of Science Kyoto Imperial University*, 8 (Series A), 291 (1925); *Koll.-Zeitschr.*, 36, 265 (1925); and *Chemical Reviews*, 2, Fig. 18-24 (1925).

† The term dilution is not meant here to be suggestive of any kind of dissolving action.

215 μμ for the second mixture.
120 μμ for the last mixture.

A. L. Stein, a student of P. P. von Weimarn, has carried out a large number of experiments [5] with crystals, both natural and artificial, and succeeded in preparing, at the suggestion and under the direction of P. P. von Weimarn, dispersoid solutions of the following substances: S, Se, Te, Sb, Au, $Al_2O_3.H_2O$ (diaspore), Fe_2O_3 (iron-glance), Cu_2S (chalcocite), PbS (galena), Sb_2S_3 (antimonite), $CoCl_2.6H_2O$ (in C_6H_6), As_2S_3 (orpiment), NaCl (in C_6H_6).

The experimental work above mentioned (N. Pihlblad, A. L. Stein *) failed, however, to give such quantitative experimental data as would comply with the requirement of P. P. von Weimarn's theory, that very highly-disperse systems may also be prepared by the method of progressive disintegration. To fill this gap, was the task suggested by Professor P. P. von Weimarn to the present author.

EXPERIMENTAL

A. Experiments at Room Temperature.

At Professor P. P. von Weimarn's suggestion, the following ten substances were taken by the author for the series of experiments here to be described: S, Se, Te, Au, Ag, Hg, $BaSO_4$, $Al(OH)_3$, Sb_2S_3 (stibnite) and denatured protein.[6]

Since the principle of P. P. von Weimarn's mechanical disintegration method implies the use of some indifferent solid dilution material, some details must first be given concerning the indifferent material used and the procedure of dilution adopted in the present experiments. In all his experiments at room temperatures and in some of the experiments at low temperatures, the author took pure anhydrous glucose (E. Merk) as dilution material; in special cases of experiments at low temperatures, pure ice prepared from re-distilled water, and sometimes urea, were also used.

In the present experiments in most instances the grinding was done by hand in an agate mortar, except that in a few cases the grinding of the mixtures was accomplished by a mechanically driven grinding machine, and the agate mortar was replaced by a silver or iron mortar. The quantities successively added of the dilution matter and the duration of grinding were as follows:

0.1 substance + 0.9 glucose ground 50 min.
0.1 of this mixture + 0.9 glucose ground 50 "
0.1 of the second mixture + 0.9 glucose ground 50 "
0.1 of the third mixture + 0.9 glucose ground 50 "
0.1 of the fourth mixture + 0.9 glucose ground 50 "

A good dispersity was obtained for Se, S and Te after grinding with the addition of glucose in the above proportions, when taken up with redistilled water.

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* Some four years after the publication by P. P. von Weimarn of his theory of mechanical disintegration (*loc. cit.*), G. Wegelin succeeded in preparing disperse systems simply by grinding with or without the addition of water the substances, *e.g.*, silicon, antimony, tungstic acid, titanic acid, molybdic acid, vanadium trioxide and melted vanadic acid; the last named substance has especially been subject to his study. He failed, however, in obtaining good results with the following substances: copper, bismuth, tellurium, selenium, sulphur, graphite, CuO, PbO_2, ZnO, CoO, Fe_2O_3, CaF_2, violet chromic chloride (*Koll. Zeit.*, **14**, 65 (1914).

As will be seen from my present publication, dispersoidal solutions of a high degree of dispersity of Se, Te and S are easily prepared by P. P. von Weimarn's mechanical method, which affords evidence that, by replacing, as G. Wegelin did, the solid "dilution matter" by a liquid one, no better results are obtained, in a general way, in the mechanical synthesis of disperse systems.

As was pointed out in my preliminary communication,[7] the dispersoid solutions obtained by the mechanical method were sometimes so polydisperse that a sediment of coarse particles could be noticed soon after the preparation; but after the complete separation of these coarse particles, long lived dispersoid solutions with fine particles remained behind. I have dispersoid selenium, tellurium, and silver solutions which still persist, and thus exhibit a stability exceeding 3½ years.*

I was able to obtain far better results with all the above ten substances when grinding the mixtures by small portions in the following way:

1st grinding: 0.9 glucose + 0.1 substance; ground 1 hour.
2nd grinding: 0.9 glucose + 0.1 of 1st grinding; ground 1 hour.
3rd grinding: about 0.2 of 2nd grinding; ground 1 hour.
4th grinding: 0.1 glucose + 0.1 of 3rd grinding; ground 1 hour.

If under vigorous stirring the powders thus obtained were brought into redistilled water, this resulted into the formation of good dispersoid solutions (especially in the case of the 4th grinding). The results of this series of experiments are given in Table I.

In view of the fact that the grinding of the mixtures was accomplished by small portions, and that also the dilution material was never added in large amounts at a time, the author was able to reach a very perfect comminution of the substance by strong and uniform grinding.

In some cases, *e.g.*, in those of Se, S and Sb_2S_3, it took about a week, up to one month, after the preparation of the dispersoid solutions, for the deposit of coarse particles to be noticed.

These facts tend to show that, under the above indicated conditions of grinding, the dispersoid solutions prepared by P. P. von Weimarn's mechanical method already approach, to a certain extent, the state of a monodisperse solution, and that anyhow they are not inferior to dispersoid solutions which were obtained by chemical or physico-chemical methods, so far as uniformity of grain and stability are concerned.

By the term "maximum stability" of the dispersoid solutions the time is designated from the moment of the preparation of the solutions up to the moment when they became transparent and showed no longer any appreciable Tyndall effect (*i.e.*, when the particles have nearly all settled down).

It will be realized from Table I and Fig. 1 that the maximum stability of the dispersoid solutions prepared by P. P. von Weimarn's method almost coincide with the highest degrees of dispersity.

The results made public earlier in my preliminary paper did not always exhibit such coincidence of the stability with the highest degree of dispersity; the solutions of the highest degrees of dispersity which were prepared in the hottest summer days, and at temperatures varying within somewhat wide limits at that, having all coagulated in comparatively short time.

So it happened that the dispersoid solenium solutions of the highest degree of dispersity attained, which were prepared during the summer, were all coagulated after two months, while those prepared in the autumn proved very stable, since they remained unaffected by such agents as heat and inconstancy of temperature.

* It must here be noted, see P P. von Weimarn and S. Utzino, *Memoirs of Kyoto Imperial University*, 8, 292 (Footnote 1) and *Koll.-Zeitschr.*, 36, 265 (Footnote 2), that the particularly high stability of the dispersoidal solutions of these three substances is due to special chemical reactions taking place between the oxide compounds of Se, Te, and Ag that were formed in the act of grinding, and the sugar.

The determination of the mean size (in μμ) of the particles was made by the well-known method of counting the number of particles present in an optically limited volume (ultramicroscope of H. Siedentopf and R. Zsigmondy) under assumption of a cubic form of the particles.

In complete agreement with Prof. P. P. von Weimarn anticipation,[8] I succeeded in reaching a size of particles smaller than the average size of dispersoid dimensions (50 μμ), except, so far, for Au and denatured protein.

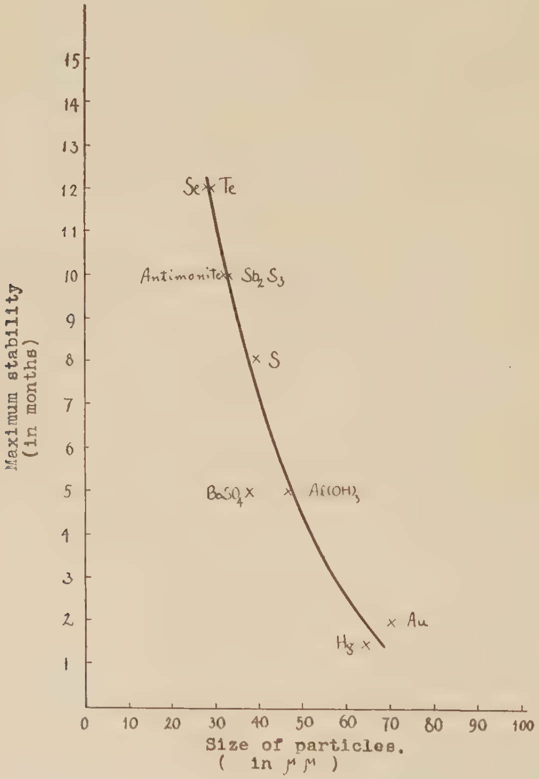

Fig. 1.—Relation between the maximum stability and the size of particles. The concentration of the dispersoid solutions was approximately the same.

It was further pointed out by Prof. P. P. von Weimarn that a series of dispersoid solutions can be prepared of gradually increasing dispersity degree, if the dilution material is added in gradually increasing amounts; this fact has been shown experimentally by the author, as may be gathered from the examination of Table II and Fig. 2. In the first four grindings, in which the amount of the dilution material added was constant, the degree of dispersity is found to increase as the time of grinding increases; and in the next three grindings, in which progressively increasing amounts of the dilution material were added, the increase in degree of dispersity is still more striking, being dependent on both the dilution and the time of grinding (Table II).

B. Experiments at Low Temperatures.

As suggested by Prof. P. P. von Weimarn,[9] the quantitative study would be both important and interesting of his mechanical method for the domain of low temperatures.

The author used, for this purpose, a cooling mixture of solid carbon dioxide and ether, and also boiling liquid air. The substance was first ground in an agate mortar, together with glucose as dilution material, at room temperature, and the last grinding was carried out at low temperature. For the grinding at low temperature mortars were used of silver, of iron and of agate and silver, dependent on the substance treated, for silver, mercury and gold respectively.

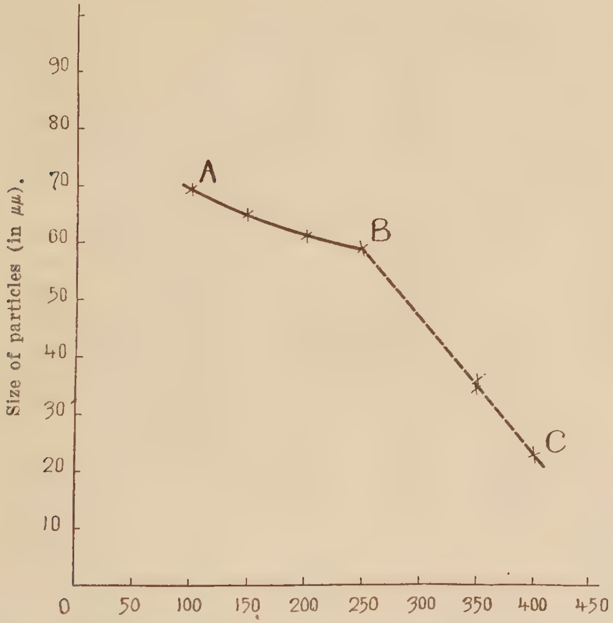

FIG. 2.—Time of grinding (in minutes). A-B—The amounts of dilution matter added were constant, only the time of grinding was increasing. B-C—Not only the time of grinding was increasing, but also the amount of dilution matter added.

Denaturated protein was first ground without the addition of dilution material at room temperatures, and subsequently with the addition of pure ice (made from re-distilled water) in an agate mortar at low temperature.

The results obtained in preparing dispersoid solutions from these powders are shown in Table III.

In this series of experiments the dispersoid solutions prepared were found to be polydisperse, since the time of grinding was comparatively short and the portions ground at a time were not very small.

Since the systems treated were of a polydisperse nature, and in consideration of the fact that the determination of the particle size was accomplished before the coarse particles had settled down, the values found may only be regarded as approximate values of the particle size.

TABLE

QUANTITATIVE DATA CONCERNING DISPERSOID SOLUTIONS PREPARED AT

1 Names of Substances Prepared in the State of Dispersoid Solutions	2 Names of Dilution Matters Ground Together with the Substances. Data Concerning Temperature	3 Dispersion Medium	4 Number of Times of Grinding	5 Sum of the Times of Grinding, in Minutes
Se (metallic crystals)	Pure anhydrous glucose of E. Merk. At room temperature.	Redistilled water (silver condenser).	4	240
Te (metallic crystals)	ditto	ditto	4	240
S (rhombic crystals)	ditto	ditto	4	240
$Al(OH)_3$ (distinct microcrystals)	ditto	ditto	4	240
$BaSO_4$ (distinct microcrystals)	ditto	55 per cent ethyl alcohol.	4	240
Sb_2S_3 (natural crystals)	ditto	Redistilled water (silver condenser).	4	240
Sb_2S_3 (artificial crystals)	ditto	ditto	4	240
Ag (silver foil)	ditto	ditto	4	240
Hg	ditto	ditto	3	The mixture was ground for 15 hours by a grinding machine and for 110 minutes by hand.
Au (gold foil)	ditto	ditto	4	240
Denatured protein (egg albumin)	ditto	ditto	4	240

I

ROOM TEMPERATURE BY P. P. VON WEIMARN'S MECHANICAL METHOD

6 Size of the Particles, in $\mu\mu$	7 Concentration of the Disperse Phase in 1 Litre of Dispersion Medium (in Grams)	8 Color of the Dispersoid Solution by Transmitted Light	9 Opalescence	10 Maximum Stability
28.8	0.0025	Orange yellow.	Quite transparent.	A smallest quantity of a deposit was remarked after 2 months. Maximum stability 1 year.
29.7	0.0025	Yellowish brown.	Quite transparent.	After 2 days a small quantity of deposit was remarked. Maximum stability 1 year.
41.7	0.0025	Reddish orange.	Faint bluish opalescence.	The first deposit of coarse particles was remarked after a week. Maximum stability 8 months.
46.7	0.0025	Colorless.	Quite transparent.	The first deposit of coarse particles was remarked after a week. Maximum stability 5 months.
38.0	0.0025	Colorless.	Transparent.	Already after 24 hours a smallest quantity of a deposit was remarked. Maximum stability 5 months.
32.8	0.0025	Yellow.	Without appreciable opalescence.	The first deposit of coarse particles was remarked earlier than in the case of artificial crystals. Maximum stability from 5 to 10 months.
33.0	0.0025	Yellow.	Without appreciable opalescence.	The first deposit of coarse particles was remarked after 1 month. Maximum stability from 5 to 10 months.
24.1 The size was determined after two weeks (sunlight illumination).	0.00125 The amount of deposit of coarse particles formed after 24 hours was determined and subtracted from the total content.	Yellowish orange.	Opalescence was remarked, which became weakened after the deposition of coarse particles.	Already after 24 hours a smallest quantity of coarse particles was deposited. Maximum stability over 3½ years.
64.6	0.00250	Brownish orange.	Faintly turbid with greyish opalescence.	The first deposit of coarse particles was remarked after 24 hours. Maximum stability 1½ months.
70.5	0.02575	Blue.	Metallic opalescence.	After 24 hours a deposit of coarse particles was remarked. Maximum stability 2 months.
ca. 100	0.0025	Colorless.	Feebly opalescent.	A very small quantity of coarse particles was remarked after 24 hours. Maximum stability 2 months.

Only in the case of silver and mercury the amount of the deposit of the coarse particles has been exactly * determined and subtracted from the total contents, when calculating the size of the disperse particles.

When the precipitate of coarse particles once settled down, the dispersoid solutions were found to exhibit a very great stability most particularly those of gold, which even now are still a splendid blue, and those of mercury which, as may be seen from Table I, used to coagulate very soon if the grinding was done at room temperature.

The present researches having been carried out in the laboratory of physical chemistry at the Kyoto Imperial University, my best thanks are due to the Director of the laboratory named, Prof. Y. Osaka.

I wish also to express my best thanks to Prof. P. P. von Weimarn, under whose direction my work was done.

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* In the case of mercury, a certain (very small) amount of precipitate was stirred up on pipetting the dispersoid solution for chemical analysis, which certainly caused some increase in concentration. We have, accordingly, to consider the concentration 0.01 gram per litre indicated in Table III as somewhat exceeding the real concentration; as regards the mean size of the disperse particles present in this solution, it does not exceed 45 $\mu\mu$, being probably considerably smaller.

TABLE II

Dispersoid Solutions of Selenium of Successively Increasing Degree of Dispersion
(Prepared by the mechanical method of P. P. von Weimarn)

Numbers and Times of the Grindings and the Amount Which Was Dissolved in 200 C.C. of Dispersion Medium	Concentration of Se in 200 C.C. Dispersion Medium (Water)	Mean Size of Particles (in μμ), Color and Stability of the Solutions
Preliminary grinding: 0.1 g. Se + 0.9 g. glucose were ground for 50 m. in an agate mortar by hand.		
1st grinding: 0.1 g. preliminary grinding + 0.9 g. glucose, ground 50 m. Amount dissolved: 0.6 g.	0.006 g.	69.5 μμ. Color: brick-red by transmitted light. A very small deposit after 24 hours. Stability over 1½ years.
2nd grinding: 0.1 g. preliminary grinding + 0.9 g. glucose ground 100 m. Amount dissolved: 0.6 g.	0.006 g.	65.0 μμ. Color: brick-red in projected light. A very small deposit after 24 hours. Stability over 1½ years.
3rd grinding: 0.1 g. preliminary grinding + 0.9 glucose ground 150 m. Amount dissolved: 0.6 g.	0.006 g.	61.4 μμ. Color: brick-red by transmitted light. A very small deposit after 24 hours. Stability over 1½ years.
4th grinding: 0.1 g. preliminary grinding + 0.9 g. glucose ground 200 m. Amount dissolved: 0.6 g.	0.006 g.	59.1 μμ. Color: brick-red by transmitted light. A very small deposit after 24 hours. Stability over 1½ years.
5th grinding: 0.3425 g. of 4th grinding + 0.6575 g. of glucose ground 50 m.	No dispersoid solution was prepared.	
6th grinding: 0.4 g. of 5th grinding + 0.6 g. of glucose ground 50 m. Amount dissolved: 0.9775 g.	0.00134 g.	35.8 μμ. Color: splendid orange, transparent. A very small deposit after 3 days. After 2 months almost all coagulated.
7th grinding: 0.5755 g. of 5th grinding + 0.4245 g. of glucose ground 50 m. Amount dissolved: 0.6 g.	0.00118 g.	34.4 μμ. Color: orange yellow, quite transparent. A very small deposit after 5 days. After 2 months almost all coagulated.
8th grinding: The residue of 7th grinding was ground 50 m. more. Amount dissolved: 0.3475 g.	0.00068 g.	22.7 μμ. Color: yellow with orange tinge; quite transparent. An insignificant deposit was remarked after a week. After 2 months almost all coagulated.

TABLE

QUANTITATIVE DATA CONCERNING DISPERSOID SOLUTIONS AT LO

1 Names of Substances, Prepared in a State of Dispersoid Solutions	2 Names of Dilution Matters Ground Together with the Substances. Data Concerning Temperature Conditions	3 Dispersion Medium	4 Number of Times of Grinding	5 Sum of the Times of Grinding, in Minutes
1 Ag (silver foil)	Pure anhydrous glucose of E. Merk. At room temperature and at low temperature (CO_2 + ether).	Redistilled water; the last time with a silver condenser.	3	200 at room temp 50 at low temp.
2 Hg	ditto At room temperature by a grinding machine and at low temperature by hand (boiling liquid air).	ditto	3 The last time in a steel mortar.	1350 at room temp 50 at low temp.
3 Au (gold foil)	ditto At room temperature. The last grinding at the temperature of boiling liquid air.	ditto	3 The last time in a silver mortar.	100 at room temp. 50 at low temp.
4 Au (gold foil)	ditto At room temperature. The last grinding at the temperature of CO_2 + ether.	ditto	5	240 at room temp. 120 at low temp.
5 Denatured protein (egg albumin)	A small quantity of pure ice. At the temperature of CO_2 + ether.	ditto	1	120

III

TEMPERATURE PREPARED BY P. P. VON WEIMARN'S MECHANICAL METHOD

6 Mean Size of the Particles, in $\mu\mu$	7 Concentration of the Disperse Phase in 1 Litre of Dispersion Medium, in Grams	8 Color of the Dispersoid Solution by Transmitted Light	9 Opalescence	10 Maximum Stability
24.8 (sunlight illumination)	0.0015 The amount of deposit formed within two weeks was determined and subtracted from the total content.	Brownish yellow.	Faint opalescence.	A smallest quantity of the deposit was remarked after 24 hours. Maximum stability of the yellow solution over 3½ years.
Not above 45 $\mu\mu$ (sunlight illumination) in the brownish-yellow dispersoid solution left behind after sedimentation of the coarse particles.	Not above 0.01. The amount of deposit was determined and subtracted from the total content.	Yellowish-brown after deposition of coarse particles.	At first quite turbid, but afterwards a feeble opalescence remained.	Coarse particles were deposited almost within 24 hours and a yellowish-brown solution remained. Maximum stability over 1 year.
85.8 There were visible very many green particles with the ultramicroscope.	0.0984	Splendid blue.	Yellowish metallic glimmer, which was weakened with the deposition of the coarse particles.	After 24 hours coarse particles were deposited and there remained a blue solution. Maximum stability 3 weeks.
68.1 This size may appear somewhat too small for the yellow particles but there were so many green particles visible that such size might be the mean value.	0.0541	Splendid blue.	Very faint opalescence.	A smallest quantity of blue colored deposit was remarked after 24 hours. The solution of a splendid blue color persisted for more than 1 year.
No exact study was carried out.	0.0560	Faint orange.	Feebly opalescent.	A deposit of coarse particles was remarked after 24 hours. Maximum stability 3 weeks.

REMARKS

(1) Ag: The last grinding was carried out at the temperature of a cooling mixture of solid CO_2 and ether. The particle size, the maximum stability and the color of the dispersoid solutions were nearly the same as those of the dispersoid solutions prepared by grinding at room temperature (Table I).

(2) Hg: The first two grindings were accomplished in a mechanically driven grinding machine, and the last grinding in a steel mortar with the hand, at the temperature of boiling liquid air. By placing the pulverized mixture in water of the room temperature, a very concentrated disperse system was obtained which was quite turbid; after, however, the coarse particles had settled down, a dispersoid solution of characteristic brownish-yellow color was left.

(3) Au: For the experiment the mixture was taken indicated in Table I; it was submitted to further grinding, first at room temperature during one hour, and then, after the addition of a certain quantity of the dilution matter, during two hours at the temperature of a cooling mixture of CO_2 and ether. The dispersoid solution obtained was a beautiful blue and proved very stable; it still retains its color though 1 year has elapsed since it was prepared.

(4) Denatured protein stuff: Well dialyzed egg albumin was caused to coagulate by heat; after washing, the coagulum was dried in a desiccator. The coagulum powder thus obtained was then allowed to freeze with a small quantity of redistilled water in an agate mortar at the temperature of a mixture of solid CO_2 and ether, and ground for two hours. By taking up the ground product with redistilled water, a dispersoid solution was obtained, faintly opalescent and faintly colored reddish-orange by transmitted light. The ultramicroscope revealed an abundance of *scarcely visible* particles.

Difficultly Soluble Silver Salts, Their Preparation and Properties

By Prof. Dr. A. Lottermoser, Dresden, Germany *

In general, when potassium iodide is permitted to react with silver nitrate, one would expect that a flocculent precipitate of silver iodide would result. That is, however, not the case. Whether or not a visible precipitate is obtained depends upon the conditions under which the reaction takes place.[1]

If 20 c.c. of a N/10 solution of KI are diluted to about one liter and if to this solution, vigorously agitated by a motor driven stirrer, we add drop by drop a N/10 $AgNO_3$ solution from a burette, no clouding of the solution takes place after the addition of the first few drops. Instead the solution takes on a greenish color. On the further addition, drop by drop, of the $AgNO_3$ solution, the solution gradually becomes more and more opalescent, until finally, when nearly equivalent quantities of KI and $AgNO_3$ are present, there is observed a rapid increase in the opalescence. However, as long as KI is still in excess no real cloudiness can be observed. The solution still remains translucent when observed with an incandescent electric lamp behind it. Cloudiness followed by gathering together of a flocculent precipitate first takes place when KI and $AgNO_3$ are present in equivalent quantities in the solution. In the example just described a colloidal solution results as long as KI remains in excess. Complete flocculation of the AgI formed will occur when the KI and $AgNO_3$ are present in equivalent quantities.[2]

Furthermore it has been found that the colloidal formation is not limited to this particular case of an excess of KI. The reaction proceeds on the whole exactly in the same way, when, for instance, 20 c.c. of a N/10 $AgNO_3$ solution which has been diluted to about one liter and which is vigorously stirred as in the foregoing experiment, has a N/10 KI solution added to it from a burette drop by drop. As long as there is an excess of $AgNO_3$ present the AgI remains in the colloidal state. As soon, however, as the $AgNO_3$ and KI are present in equivalent quantities complete flocculation of AgI takes place.[2]

The question now arises as to what causes underlie the formation colloidal AgI. If we examine the colloidal solution obtained in the presence of an excess of KI as to its behavior in electrophoresis, we find that the AgI travels towards the anode and therefore carries a negative charge. Similarly examination of the colloidal AgI solution prepared in the presence of an excess of $AgNO_3$ shows that in this case the colloidal AgI carries a positive charge, for it travels towards the cathode. The reaction can be considered as taking place as follows:

$$KI + AgNO_3 \rightleftarrows AgI + KNO_3.$$

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* Translated by Dr. Julius Alsberg, New York.

However, as in each case, regardless of whether KI or AgNO_3 is in excess, KNO_3 results during the conversion, the latter can play no significant part in the formation of the colloid. It is, therefore, more correct to consider the reaction as an ion reaction as follows:

$$\text{I}^- + \text{Ag}^+ \rightleftarrows \text{AgI}.$$

It is now at once clear that, with KI in excess, the *iodine ion* will bring about a negative charge, and that with excess of AgNO_3 on the other hand the *silver ion* will bring about a positive charge of silver iodide; *i.e.,* in the first case the AgI as the dispersed phase adsorbs the I from all the molecular forms present in the solution; similarly in the second case it adsorbs the Ag^+. We can, therefore, schematically formulate the negatively charged colloidal silver iodide as follows:

$$(x\text{AgI})\text{I}^- + \text{K}^+$$ [3]

or taking into consideration also the adsorption of the remaining kinds of molecules:

$$\begin{pmatrix} x\text{AgI} & \\ a\,.\,\text{KI} & b\,.\,\text{KNO}_3 \end{pmatrix} \text{I}^- + \text{K}^+.$$

i.e., we can consider it as an electrolyte with a strong complex anion and a simple cation. Analogously the schematic formula for the positively charged AgI sol will be as follows:

$$(y\text{AgI})\text{Ag}^+ + \text{NO}_3^-$$

or more exactly

$$\begin{pmatrix} y\text{AgI} & \\ c\text{AgNO}_3 & d\text{KNO}_3 \end{pmatrix} \text{Ag}^+ + \text{NO}_3^-.$$

The difference between such complex *colloidal* ions and the hitherto known complex ions is very considerable. In the case of the latter there exist, under all conditions, stoichiometric relations of a simple character between the neutral part and the complex formation. For instance, in the ions AgI_2^- there exists the ratio of $\text{AgI} : \text{I}^- = 1 : 1$ and for AgI_4^{---} the relation of $\text{AgI} : \text{I}^- = 1 : 3$ or in the ion Ag_2I^+ the relation $\text{AgI} : \text{Ag}^+ = 1 : 1$. In the case of the former the relation or ratio can have any possible value, and x and y can reach very great values.

There is one further condition that must be satisfied in order that AgI may form a hydrosol during the inversion of I^- and Ag^+. A certain total concentration of the solution must not be exceeded. This concentration limit, above which a precipitate of AgI at once forms, depends upon the nature of the other ions present in the solution. If silver nitrate is permitted to react with potassium iodide, a hydrosol can already be obtained with a N/8 solution of KI. If, however, barium iodide or cadmium iodide is employed in place of potassium iodide, the concentration must be reduced to N/100 to obtain a hydrosol. At the same time Ag_2SO_4, to the extent that its smaller solubility will permit, can replace AgNO_3 without detrimental result.

When on the other hand iodine ions are added to an excess of silver ions, it makes no difference whether solutions of potassium iodide, barium iodide or cadmium iodide are employed. When their N/20 solutions are added to N/20 silver nitrate solution, an AgI hydrosol results. If, however, we substitute silver sulphate for silver nitrate there results at once, even with N/100 solutions, a precipitation, *i.e.,* a gel formation.[4]

These observations are in complete accord with the well known law that negatively charged sols are the more readily precipitated by electrolytes, the greater the valency of their cations; that, therefore, their precipitation threshold value decreases rapidly with increase in valency of the cation; and that, conversely, positively charged sols are especially sensitive to the action of electrolytes with polyvalent anions. We will again observe this rule in the case of ion reactions which result in other difficultly soluble silver salts.

If now we compare the reaction between I^- and Ag^+ in case A (where iodine ions are in excess), with case B (where silver ions are in excess) we find, as is clear from the maximum concentrations given, that the negatively charged AgI sol is more stable than the positive AgI sol. The former can form in much greater concentration than the latter. Furthermore it is found that in general sol A requires fewer iodine ions for its existence than sol B requires of silver ions; that in case A the floc formation approaches more closely to the equivalent point $I^- + Ag^+$ than in case B, where the floc formation begins sooner.

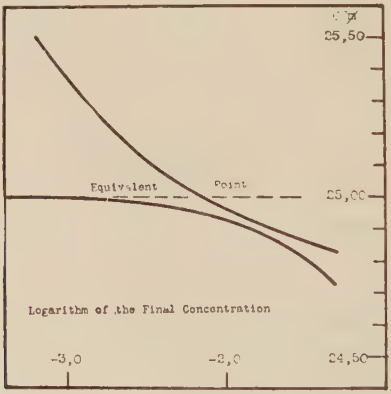

FIG. 1.

When flocculation begins it does not follow that it is complete; *i.e.*, after the settling of the floc the supernatant solution is not necessarily completely clear. The point of complete clarity comes after the point where precipitation begins. This point of complete clarity exhibits a peculiar trend with decreasing concentration of the reacting solutions. In general it can be stated that, with decreasing total concentration, the quantities of silver nitrate and potassium iodide required respectively for cases A and B increase, but that the quantity required for B always is less than for A. The following curve, which holds for not too great a speed of stirring, illustrates the relationship. The increase in amount of solution used with increasing dilution is clearly indicated. In case B the values lie in a curve which is asymptotic to the equivalent point, while in case A the value rises far above this, without being able to show the presence of an excess of silver nitrate in the clear solution. That is the reason why the point of clarity coincides with the point of electrometric reversal, *i.e.*, with the greatest change or jump of potential, when the titration is carried on during continual measurement of the potential Ag/Ag^+. This shifting of the point of clarity and electrometric reversal with the concentration of the solutions employed, is no doubt due to the adsorptive action of the silver iodide, which naturally depends upon the concentration. If the stirring is carried on at the highest possible speed, the curve for case A assumes a direction similar to that already obtained for case B, namely, asymptotic to the equivalent point (see Figure 2).[5]

However, attention must be called to the fact that, with rapid crossing of the equivalent point, that is with a rapid addition of an excess of silver nitrate solution, of not too great a concentration, to a negative AgI sol or of an excess of potassium iodide to a positive hydrosol, no precipitation takes place, but instead merely change of charge of the hydrosol. In such case the coagulation, which requires a definite period, has not the time required for its formation.

If now we compare the results found in the case of silver iodide with the results that were obtained in the case of the reaction between silver ions and other anions which yield difficultly soluble silver salts we find the following:[6] The reaction between bromine ion and silver ion takes place exactly the same as that between iodine ion and silver ion. In this case, too, the positively charged silver bromide sol is less stable than the negatively charged one. Also the reaction between chlorine and silver ion falls in line here, only the relationship becomes more uncertain. Instead of forming a negatively charged sol, more frequently a fine cloudiness results, since the solubility of AgCl lies at about the limiting value where sol formation still takes place without the formation of coarser crystals. In the case of positively charged AgCl sol this is not so plainly evident. It can be considered more stable than the negatively charged one. Sulphocyanide of silver in its behavior resembles more nearly bromide of silver. In place of the potassium, sodium and ammonium salts of the hydrogen-halogen acids with which may also be included HSCN, we may employ the free acids without noticing any change in the phenomena. In the case of the positively charged sol, *i.e.*, with an excess of Ag^+, this is not surprising. But in the case of the negatively charged sol we face an anomaly, since negatively charged sols as a rule are very sensitive to the influence of hydrogen ions. This phenomenon undoubtedly is due to the fact that in the case under consideration the halogen silver compounds adsorb H^+ only very weakly, whereas other highly negatively charged sols strongly adsorb the latter. It has already been stated that many valent cations have a strong precipitating action. The substitution for Ag^+ of $Ag(NH_3)_4^+$ does not have a detrimental influence on the formation of the AgI negative sol. However, with an excess of silver salt, *i.e.*, in case B, and with higher concentrations, this substitution prevents entirely

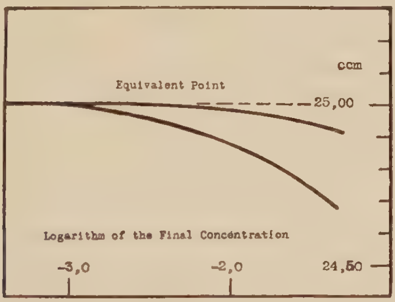

FIG. 2.

the formation of any hydrosol. This is due to the excessive concentration of OH^- ions in the solution. The same phenomenon can be observed when silver nitrate solution is titrated with a potassium hydroxide solution. Curiously, with an excess of potassium hydroxide solution (in titrating with silver nitrate solution) a hydrosol is formed only at very great dilutions and even then precipitation occurs at a point considerably in advance of the equivalent point.

It is mostly impossible to form a positively charged sol with salts of polyvalent anions, which form difficultly soluble silver salts; or at least only in the extreme dilution of the solutions. This becomes more and more pronounced as the valency of the anion increases, and is especially striking with ferri- and ferro-cyanide ions. However, the solubility of the particular silver salt in question also has a decided influence. With decreasing solubility the effect of polyvalent anions becomes more pronounced. A positively charged silver sulphide sol cannot be prepared at all or only in extreme dilution and the point of precipitation here lies far ahead of the equivalent point $2Ag^{+}+S^{--}$. Furthermore with negatively charged silver sulphide sols the relationship is far from definite. An exact titration of S^{--} with Ag^+, using the point of clarity as the end point of reaction, is not possible. Frequently, for reasons unknown, the precipitation occurs much too soon. These same irregularities are also apparent when we attempt the electrometric titration of sulphur anion with silver nitrate. The titration is quite impossible.

The hydrosols of difficultly soluble silver salts may be considered as typical hydrophobe sols, as their composition is accurately known. Consequently they can be used to obtain a clearer and deeper insight into the effect of electrolytes on colloidal solutions. The best for this purpose is silver iodide or bromide hydrosol; firstly because these sols are very stable and secondly because they can be prepared with negative as well as positive charge. Consequently it becomes possible to study the mutual effect of positive and negative hydrosols.[7]

As is well known, Buxton and his co-workers[8] discovered a series of different types of coagulation from hydrosols. In part at least these had been previously observed by other workers. These various types of coagulation can be reproduced with silver iodide sols. The first type, as established by Buxton, is that in which flocculation is brought about by means of electrolytes. In this type precipitation of the hydrosol is brought about beginning with a definite concentration value of the added electrolytes, called the *threshold value*. All concentrations above this value up to the highest also bring about coagulation. The concentration of the hydrosol is not a factor. This type already makes its appearance with the conversion of I^- with Ag^+. Above a definite concentration of the added potassium iodide solution, in the case of negative silver iodide sol, coagulation of the AgI occurs instantly. Similarly, with positive AgI sol, beginning with a definite concentration of silver nitrate solution and upwards, only a gel formation is observed. But negative and positive silver iodide that have already been prepared also show this type of precipitation with electrolytes such, for instance, as acids, or alkali nitrates. This type is graphically illustrated in Figure 3 taken from Buxton.

A second type of coagulation is colloidal precipitation. In this case a definite quantity relationship (by weight) of two oppositely charged hydrosols must exist to bring about coagulation. In the presence of an excess of either of the two hydrosols, precipitation does not occur, and the mixture possesses the properties and therefore also the charge of the hydrosol present in excess. Buxton represents this type of precipitation by Figure 4. This type of precipitation can be well reproduced with negative and positive silver iodide sol. At the same time it is found that the point of maximum precipitation in the precipitation zone is not dependent upon the amount of AgI in the hydrosol. It depends upon the excess quantities of iodine and silver ions present respectively in the negative and in the positive sols. These excess quantities must be equivalent for a maximum precipitation effect.

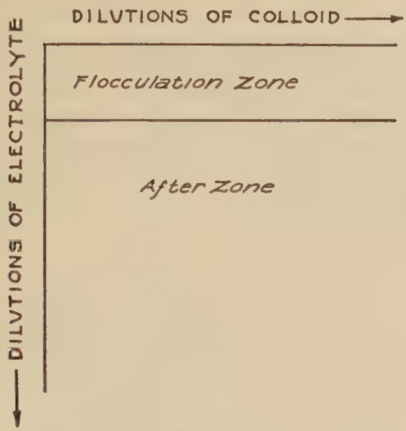

FIG. 3.

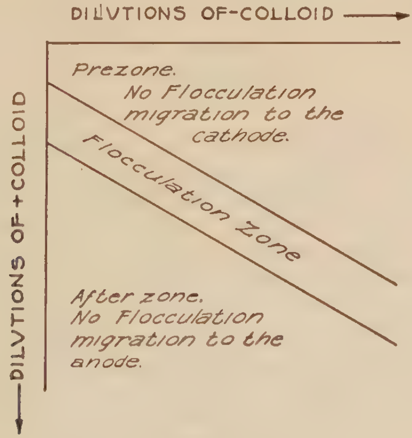

FIG. 4.

This behavior of oppositely charged AgI sols is in complete agreement with the effect of positively charged iron oxide sol on negatively charged stannic oxide sol as shown by the quantitative experiments of Wintgen. In the latter case precipitation occurs, not when equivalent quantities of Fe_2O_3 and SnO_2 are brought together, but *when the ions present* in each sol which determine the charges of the hydrosols and also the compensating ions present in the solutions, are equivalent to each other. However, Buxton[9] had already recognized that the colloidal coagulation zones can widen in one direction and always in that direction where the less colloidal sol is present in excess. Thus in the case where negative acts on positive AgI sol, the coagulation zone is broadened in the direction of the excess of the less stable positive sol, and the further the more dilute the negative AgI sol employed.

And finally there is a third type of coagulation which covers the so-called irregular series. These have been carefully investigated by Bechhold.[10] These irregular series, up to the present, have been observed only in the case of negative hydrosols. According to Buxton their behavior is represented by the diagram in Figure 5. It shows that small quantities of the indicated electrolyte do not bring about precipitation, and leave the properties, including the charge of the hydrosol, unchanged. Adjacent to this lies the zone of colloidal flocculation, in which a definite relationship of the amounts of colloid and electrolyte is required for flocculation. Next to this zone of flocculation lies a second zone of non-flocculation, in which the hydrosol is changed over to a positively charged one. And finally the phenomenon ends in an electrolyte-flocculation zone, in which only the concentration of the electrolyte, and not that of the colloid, governs. In the case of a negative hydrosol only such electrolytes can give rise to irregular series, as are hydrolytically split, and as a result of the hydrolysis give rise to a positively charged sol. Examples of such electrolytes are ferric, aluminum and chromium chloride, thorium nitrate, etc. If now we examine the effect of silver nitrate solution on a negatively charged silver iodide hydrosol, we find the following. A very small quantity of a very dilute silver nitrate solution does not flocculate the sol. The latter remains negatively charged. A quite appreciable amount of a silver nitrate solution will flocculate an appreciable amount of the negative AgI sol only when the quantity of the silver ions is exactly equivalent to the quantity of iodine ions present in the sol. The result depends not upon the concentration of the components, but upon the quantity relationship. If silver nitrate solution be added in an excess, which however must not exceed a very definite concentration, to negative AgI sol, no flocculation takes place, but there results a change in charge to positive silver iodide sol. After

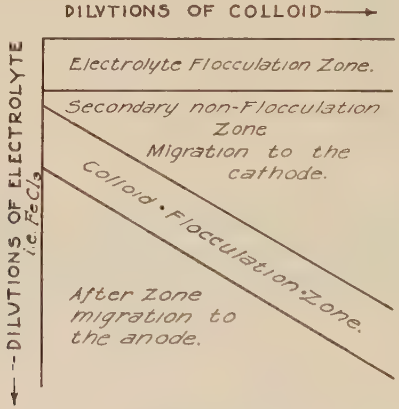
DILVTIONS OF COLLOID
DILVTIONS OF ELECTROLYTE i.e. FeCl3
Electrolyte Flocculation Zone.
Secondary non-Flocculation Zone
Migration to the cathode.
Colloid • Flocculation • Zone.
After Zone migration to the anode.

FIG. 5.

this has taken place, as much of the silver nitrate solution of the same concentration can be added as may be desired without bringing about flocculation. On the contrary the positive sol becomes rather more stable. However, beginning with a definite concentration, silver nitrate solution up to the highest concentrations will flocculate negatively charged AgI hydrosol irrespective of the concentration of the latter.

Although, as has been previously stated, irregular series have up to the present not yet been observed in the case of positive hydrosols, nevertheless exactly such an irregular series can be brought about, as in the case of silver nitrate solution and negative silver iodide sol, by the action of potassium iodide solution on positive silver iodide sol. The positive sol in this case is converted to the negatively charged one in the secondary non-flocculation zone.

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The Constitution of the Dispersed Micell in Platinum Electrosols

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In order to study the mechanism of chemical reactions activated by colloids, it is necessary to know precisely the constitution of the dispersed micell in these systems. By following, as far as may be, its changes in constitution in the course of catalytic phenomena, we may find out the basic principles on which these catalyzers work, which are no doubt of a chemical nature because their catalytic power does not reside in units of the physical order met with in the study of colloids.[1]

But a study of the chemical constitution of dispersed particles in colloidal systems is a problem full of difficulties, for colloids are in their very nature very unstable systems from a chemical point of view. The micell, insofar as it has the properties belonging to colloids, is a chemical complex which is the seat of incessant transformations, activated or retarded by numerous causes which, in consequence, produce variations in these systems whereby the dispersed phase tends to lose its characteristic properties.

We have attempted in several cases to solve the problem of the chemical constitution of the dispersed particle in colloidal systems; but we shall here refer to only one case, that of electrosols of platinum dispersed in oxygenated water.

When platinum is electrically atomized in water, according to the well-known method of Bredig, tiny bubbles of gas are liberated, whose origin is, we think, due to dissociation of the water by the electric sparks spitting in the midst of it. We believed that by studying this gas, important conclusions might be deduced as to the chemical constitution of the dispersed micells of the electrosol, and to this end we made several series of experiments.

In order to collect this gas we caused the electric sparks to jump between platinum electrodes immersed in water, placing the arc within a funnel or bell which terminates in a endiometric tube as shown in Fig. 1.

Having obtained enough gas to study (10 cc.), we made some sparks jump between the platinum terminals fused into the upper part of the tube. The volume of the gas did not show sensible change. Therefore it was no mixture of hydrogen and oxygen, although both are evidently formed by decomposition of the water by the spark at the moment when the electrosol is formed.

We examined the gas collected: (1) by introducing into it tiny cylinders of yellow phosphorus—after fifteen minutes the volume of the gas had not sensibly changed; (2) by mixing with the gas a known volume of hydrogen and sparking the mixture—the volume did not change. These experiments indicate that the gas contains no oxygen.

* Translated by Jerome Alexander.

Continuing the experiments, we introduced some oxygen into the tube. The mixture produced diminished in volume on contact with the colloid, for the platinum electrosol catalyses the synthesis of water. We repeated this experiment several times and studied it quantitatively.[2] From all this we conclude that the gas originally collected was hydrogen.

Now this hydrogen evidently came from the dissociation of the dispersion water, and therefore the oxygen simultaneously formed remained united with the platinum micell, for it could not be dissolved in the water since this was initially saturated with oxygen.

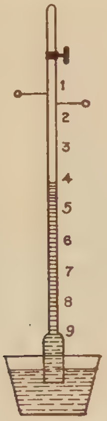

FIG. 1.

To see if the platinum micells retained the oxygen corresponding to the hydrogen collected, we allowed two liters of the platinum electrosol to coagulate spontaneously, collected the coagulum and dried it at ordinary temperature in a calcium chloride desiccator. We examined the dried coagulum by placing a known weight of it in a horizontal tube connected at one end with a tube for disengaging gas, and at the other with a U tube to dry the carbonic gas liberated by the triple-mounted bottle (see Fig. 2).

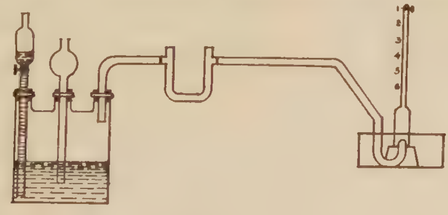

FIG. 2.

Proceeding with due care, after the air had been driven from the apparatus the coagulum was heated to a dull red. A quantity of gas, which was not absorbed by the concentrated sodium hydroxide solution filling the collection tube, collected in the graduated tube. This gas proved to be oxygen. This experiment in conjunction with those previously described show that the dispersed micells in platinum electrosols do not consist of pure platinum, but of this metal combined with oxygen.

The quantity of oxygen thus combined with the platinum varies greatly according to factors as yet undetermined; among them are the current, distance between the electrodes, purity of the dispersing water.*

The following is one series of determinations:

Weight of Pt Atomized	Vol. of O Absorbed	Vol. Ratio Pt: O
0.0284 grams	0.5 c.c.	1:378
0.0351 "	0.5	1:306
0.0375 "	0.5	1:286
0.0382 "	0.5	1:281
0.0425 "	0.5	1:252
0.0527 "	0.5	1:204
0.0772 "	0.5	1:139
0.1281 "	0.5	1:83
0.1400 "	0.5	1:76

The following experiments were made to check the conclusions described above. In the presence of sulphuric acid, platinum electrosols (like ozone) decompose solutions of potassium iodide, liberating iodine. Using known solutions of potassium iodide and platinum electrosols having a known amount of platinum, we estimated the *active* oxygen fixed by the micell by determining the amount of iodine liberated by titration with sodium thiosulphate.

Numerous experiments for determining the oxygen in platinum electrosols by this volumetric method, led to an interesting conclusion: the quantity of oxygen thus determined is about half of what the electrosol should contain, calculated on the basis of the amount of hydrogen set free when the electrosol was formed. Taking sols made with a current of 2.9 amperes and 90 volts, the following results were found on comparing the quantity of oxygen determined by these two methods:

Vol. of Dispersion Water	Pt. Atomized in Mg.	C.C. of O Fixed per Mg. Pt.	C.C. of O Determined Volumetrically, per Mg. Pt.
200 c.c.	21.0	0.0238	0.0112
200 c.c.	9.5	0.0278	0.0113
400 c.c.	13.9	0.0359	0.0192
400 c.c.	22.6	0.331	0.0169

In several previously published papers [3] we think we have shown that the oxygen united with the platinum micell is the active agent in catalytic reactions in which this colloid takes part, so that the catalytic power of platinum electrosols is intimately connected with the amount of oxygen fixed by the micells.

In short, the platinum particle is the support for a platinum-oxygen system formed at the micellular surface. From this point of view metallic colloids are allied to biochemical catalysers which also operate in colloidal state. Thus diastases have an organic particle (support) at the surface of which are adsorbed the ions which are the active agents in biochemical catalysis.

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* If this is an adsorption phenomenon, the degree of dispersion of the platinum is most important. J. A.

Pyrosols

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1. General Introduction and Basic Experiments With Metal-Fog †

In 1893, while experimenting on the electrolysis of molten salts, Richard Lorenz noticed a phenomenon to which he gave the name metal-fog (metallnebel). This discovery has proved of fundamental importance in the field of electrochemistry at high temperatures, and of significance in the fields of colloid chemistry, of mineralogy, of photochemistry, and of chemical technique.

Observation of the electrolysis of molten salts in transparent vessels, which was carried out again by Lorenz for the first time since the work of Faraday ‡ made it possible to recognize the metal-fog unmistakably. By way of example, in the electrolysis of pure molten cadmium chloride (anhydrous) in a hard glass test-tube,[1] we see that gaseous chlorine forms at the anode, while at the cathode there form heavy, dark-brown clouds, which move about in the melt and finally color it completely brown, whereas pure cadmium chloride is colorless when melted. The reduced metal falls to the bottom of the container, although in small quantities. The major part of the cadmium goes into the brown mist clouds, which move about in the melt. After solidifying, the fused mass looks gray, and after extracting with water we can isolate a very fine crystalline powder consisting of thin leaves, which proves to be metallic cadmium. Molten zinc chloride shows exactly the corresponding phenomena, and on electrolysis yields a suspension of metallic zinc similar to zinc dust.[2]

Jointly with V. Czepinski, O. H. Weber, and A. Helfenstein in 1898-1899 Richard Lorenz observed the formation of metal-fog during the electrolysis of salts of lead, tin, bismuth, and silver, and investigated especially the disturbances caused by this metal-fog; these occur during the electrolysis of the molten halides of the heavy metals and decrease the yield of the current. It developed that it is not the freed stream of halogen diffusing through the molten mass that reduces the yield,§ since this stream passes from the anode to the cathode as already mentioned. Metals migrate in molten electrolytes generally in the form of metal-fog from the cathode to the anode, where they recombine with the halogen (for example, chlorine) to regenerate the original salt.[3]

Especially important is the establishment of the fact that metal-fog occurs independently of the electrolytic process merely through the bringing together

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* Translated by Evelyn Sommerfield, A.B.

† I owe sincere gratitude to my friend Professor W. Eitel of Königsberg, who assisted me in the writing of this article.

‡ Bunsen himself performed his masterly work on the electrolysis of molten salts mostly in crucibles.

§ As Bunsen had already assumed in his classic experiments in the electrolysis of molten salts.

of molten chlorides (bromides, iodides, etc.) with molten metal. Thus R. Lorenz and A. Helfenstein demonstrated in 1900 at the seventh general meeting of the German Electrochemical Society[4] how, on the introduction of a metal (*i.e.*, lead) into the melt of its chloride (*i.e.*, lead chloride), from the surface of the molten regulus inside the colorless molten chloride, a fog arises often with even explosive violence, distributes itself in the molten mass and gradually stains it deeply. By prolonged heating one can reach a definite point where the chloride is saturated with metal-fog; at this point the melt is of a very dark color and opaque. On gradual cooling, the phenomenon disappears again: the metal regulus absorbs the fog to some extent. On sudden cooling of the foggy molten halides one obtains gray masses of crystals.

These solutions and dispersions of a metal in its molten salts R. Lorenz (1910[4]) called *"pyrosols,"* for he felt that on account of the intense color effects shown, this metal-fog must correspond to ordinary metal sols and might be equally complex. Because of the high temperature of the dispersion medium (here the molten salts) they differ from ordinary sols, as is indicated by the πῦρ = fire. The phenomenon of metal-fog is dependent to a quite remarkable extent on the vapor pressure of the metallic substances, which are in suspension in the melts. Bromine layered under water gives off its vapor into the water, and after a certain period bromine vapor is given off from the surface of the liquid. A similar condition exists with metals in the melts of their salts: they give off their vapors into the melts, and under some circumstances these vapors pass through the melt into the atmosphere. One can observe this particularly well with cadmium in cadmium chloride. And just as bromine is partly dissolved as such in water, and at the same time shows a partial tendency to form certain combinations with the solvent, such is likewise the case with solutions of metal in molten salts. On supersaturation, condensation takes place in the form of colored streaks and clouds (metal-fog). We see, therefore, that the phenomenon of pyrosols is a complex one.[5] *The formation of metal-fog in melts, the solubility of the metals in the melts, the evaporation of the metals from the melt, the possible formation of lower chemical compounds* (subchlorides, etc.) *which are in equilibrium with the metallic solution and other components of the melt—all this forms a complex of related facts, which is to be compared with the complex phenomena of the colloid chemistry of aqueous solutions.*

The portion of this complex phenomenon first known, is that connected with the formation of lower compounds (subhalides). Formerly all phenomena exhibiting themselves during the electrolysis of molten salts as overvoltage, current losses, were attributed to "subhalides," which, it was assumed, formed as a result of the action of metal on the molten salt involved. Holding this point of view, H. Davy, in his electrochemical investigations, was the first to show that metallic potassium heated with potash forms masses varying in color from red-brown to gray, which he called combinations corresponding to suboxides. The same substances form on the electrolysis of potash with a strong current and high temperature. Bunsen and Kirchoff noticed losses of current on electrolysis of rubidium chloride and caesium chloride which they ascribed to the formation of a blue subchloride. By melting metallic potassium with potassium chloride in a stream of hydrogen, H. Rose was able to produce the same deep blue substances. Sodium and sodium chloride behave similarly. Setterberg attributed the facts observed on electrolysis of caesium chloride to the formation of a subchloride. While in the earlier statements about subhalides many obscurities and uncertainties prevail, through several recent investigations the existence of various subhalides, as it seems, has been securely established.

A simple solubility of metals in molten salts was, as already mentioned above, postulated by Lorenz, in connection with colloidal metal-fog. The possibility of such a solution had been previously denied (see below). As we shall see later, this hypothesis can no longer be rejected out of hand. In his investigations, Lorenz conceived this solubility and the formation of colloidal metal-fog to be a *single* (complex) phenomenon, and called whatever metal passed into the molten salt (including even subhalides formation) as "soluble," in the sense of the language of the older colloid chemistry. The determination of the quantities of metal dissolved in molten salts as pyrosols, was first carried out by Lorenz and Helfenstein, who showed that very small quantities of metal may give rise to the color. The solubility of the metals in the chloride melts busied Lorenz fully as early as 1900, and more recently the solubilities of sodium and potassium in molten caustic alkalies has been minutely investigated by G. Meyer and G. von Hevesy.[6] A. H. W. Aten[7] has discussed the question of the solubility of metals in the melts of their salts from the standpoint of conductivity. However, Lorenz, von Hevesy and Wolff[8] succeeded in determining directly the concentration of the metals in the chloride melts by a sort of titration. Furthermore, pyrosols can be produced by purely chemical methods, by reducing molten salts without the addition of regulus metal. On the other hand, the addition of foreign salts, *i.e.*, alkali chlorides, to molten salts of the heavy metals hinders the formation of metal-fog in these melts, as Lorenz, H. Frei, A. Appelberg, and the above mentioned collaborators showed. Melts already cloudy, lose their fog on such additions. This behavior of pyrosols suggests "salting out" in aqueous colloidal solutions, without perhaps being identical with it. In connection with this the investigations of R. Lorenz and G. v. Hevesy, F. Kaufler, E. Wolff, A. Liebmann and A. Höchberg in the years 1908-1911 may be mentioned, which indicate the connection of metal-fog with the surface tension of the metal regulus in contact with the salt melt. Here also we find certain analogies between the pyrosols and aqueous colloidal solutions.

The analogy of metal-fog coloration with certain phenomena of the colloid physics of solids is of great scientific interest, especially the analogy with dilute mineral colors, with salts colored by cathode and radium rays, and with the glass colored by metals (particularly gold and copper). Here the well-known investigations of R. Zsigmondy found important confirmation through the discovery of the metal-fog phenomena. Ultramicroscopic investigations of metal hydrosols by Zsigmondy, the study of gold ruby-glass (Zsigmondy) and of natural blue rock salt (Siedentopf), showed the presence of finely dispersed metallic particles. After all these analogies, there remained hardly a doubt that pyrosols and the systems represented by their chilled products were anything else but colloidal metal suspensions in a molten or a solid medium. The presence of ultramicroscopic fog particles in the chilled melts of the halides of lead, silver, and thallium, was ultramicroscopically demonstrated in the years 1914 and 1915 by R. Lorenz, W. Eitel and K. Hiege.*

Aside from the interest that the liquid pyrosols possess for such scientific questions as the solubility of metals in liquid melts, the existence of a colloidal state at higher temperatures, and the chemistry of lower compounds, they (the pyrosols) have also outstanding technical significance. R. Lorenz and his numerous collaborators showed that the electrolysis of molten salts is controlled decisively by pyrosols. The presence and the formation of pyrosols (metal-fog) clarifies our understanding of current yield. By help of a knowledge of pyrosols we arrive at a quantitative theory of these phenomena. While, after Faraday's investigations, it might still be uncertain whether the law of strict electrolytic action at higher temperatures holds rigidly, investigations concerning the connection of pyrosols with these phenomena of electrolysis prove the complete and exact validity of this fundamental law in the field of higher temperatures; and it could be proved that the losses in current and material are due solely to the presence and properties of pyrosols. Such knowledge is of the greatest technical importance, since it is possible on such a basis to improve systematically and practically electrolytic processes involving liquid melts. Through consideration of the facts about pyrosols the current yield has been constantly increasing in the most diverse kinds of factories in Europe and America. Both the theory and practice of additions to the melts developed from the theory and properties of pyrosols. Besides the electrochemical field, involving current strength, the pyrosols are of importance in the field of electromotive force in molten systems which is strikingly dominated by them. For pyrosols act at the anode (in contradistinction to the halogens) as excellent depolarizers. Therefore the electromotive force at the anode is changed. The phenomena of polarization, decomposition pressure, and overvoltage in molten electrolytes are dependent on the presence and properties of pyrosols.

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* In the melée of molecules, atoms and ions, if there are present an excess number of metallic atoms or ions (because of addition of metal, or elimination of halogen), these metal particles may be adsorbed at the surfaces of the halide crystals or particles. The slower the chilling, the greater the segregation of metal and of halide. Analogous phenomena occur in metals and alloys. J. A.

In photochemistry the solid as well as the liquid pyrosols possess scientific and technical interest. Metal-fog has been of especial importance in throwing light on the nature of the latent photographic image, as is expressed in the silver-germ theory. By 1900 R. Lorenz reached the conclusion that the latent photographic image could be nothing other than a very finely divided suspension of metallic silver in a silver halide ($AgCl$, $AgBr$). He therefore became an advocate of the silver-germ theory proposed as early as 1887 by R. Abegg, that meanwhile has been abandoned in favor of the subhalide theory, according to which the first ray of light that strikes the sensitive photographic layer of silver-salt emulsion produces a partial reduction of the silver halide (*i.e.*, $AgBr$) to subhalide (*i.e.*, Ag_2Br). The validity of the silver-nucleus theory is favored by the observations of R. Lorenz, W. Eitel and K. Hiege, who observed in optically empty crystals of silver halides the development and rapid growth of tiny silver particles visible in the light beam of the ultramicroscope.

2. SUBHALIDES

Heretofore during the electrolysis of liquid melts the manifold forms of metal-fog were confounded with the reactions which occur in such melts as a result of their hygroscopicity, or the erroneous attempt was made to explain the poor yield, current losses, convection currents, for example with chlorides, entirely by the diffusion of the chlorine evolved at the anode from the anode to the cathode. Also on account of the then prevailing uncertainty as regards valence, scientists were immoderately inclined to assume the formation of lower chemical compounds whenever metal-fog made its appearance. They hardly considered it necessary to prove the existence of such compounds.

Thus numerous articles on the formation of subhalides were printed in the text-books without verification, just as though they dealt with well proven facts.

It has been above mentioned that H. Davy in his electrochemical investigations[9] concerning the electrolysis of potash, was the first to obtain brightly colored masses, which he called a "suboxide" of potassium. Similarly Bunsen and Kirchoff[10] were of the opinion that one must assume the formation of subchlorides of rubidium and caesium during the electrolysis of rubidium chloride and caesium chloride. H. Rose[11] was able to obtain the same deep blue substances by melting metallic potassium with potassium chloride in a stream of hydrogen; with sodium and sodium chloride he found corresponding blue masses of a salt, the color of which he attributed to the probable formation of Na_2Cl. Finally Setterberg,[12] during the electrolysis of caesium chloride, noticed a dark brown stream originating at the negative electrode, which distributed itself throughout the blue melt of caesium chloride.

In electrochemical literature, as for example, in Borchers[13] we often find the losses of current and the deficient yield of the current in the production of the alkali metals from the chloride melts was attributed to the formation of subhalides. On the contrary, the more recent observations of Stockem[14] are important, for they show that the chloride containing metallic sodium crystallizes regularly like the pure chloride, and hardly a tenth of the sodium necessary for the formation of a subchloride is dissolved. Guntz[15] mentions a subchloride of lithium, Li_2Cl. All these phenomena are fully explained through the formation of metal-fog in the halide melts.

The evidence as to the formation of well-defined subchlorides of calcium, strontium, and barium seem better grounded. Borchers specifies[16] that a portion of the metallic calcium formed during the electrolysis of molten calcium chloride redissolves in the melt as subchloride. With Stockem this same author[17] holds that a red crystalline layer of salt is found on the electrolytically separated calcium, and Klockmann found this layer fully transparent, with vivid pleochroism ranging from red to violet. The crystals are monoclinic or rhombic. Analysis showed an approximate formula Ca_2Cl_2. Ruff and Plato[18] also obtained a subchloride of calcium, as did Guntz[19] in his double halides of barium and sodium salts of the type [BaCl.NaCl], [BaF.NaF], [BaBr.NaBr], [BaJ.NaJ], W. Hampe and W. Diehl[20] ostensibly obtained a compound of aluminium containing less fluorine than the formula AlF_3 indicates.

Especially important for metal-fog research are the reports of H. N. Morse and H. C. Jones[21] concerning the formation of halides of a lower order from cadmium salts. If pure cadmium chloride with an excess of metallic cadmium is heated to the melting point in an atmosphere of nitrogen, it acquires a deep garnet-red shade. The composition of the crystals obtained from the melt corresponds exactly to the formula Cd_4Cl_7; when treated with water, $CdCl_2$, goes into solution, and there remains a residue supposed to be subhydrate CdOH. Cadmium bromide showed similarly a mass designated as subbromide Cd_4Br_7, while from cadmium iodide a subiodide was derived with the formula $Cd_{12}I_{23}$. Morse and Jones assume that the bodies analyzed represent saturated solutions of the subhalides CdCl, CdBr, CdI in $CdCl_2$, $CdBr_2$, and CdI_2. The interpretation of these phenomena through the formation of metal-fog with its resulting equilibria, is due to the investigations made by R. Lorenz and his students.

The sensitiveness of the silver (and thallous[22]) halides was ascribed to the formation of subhalides of the sort Ag_2Cl, Ag_2Br, Ag_2I. Up to the present only the silver subfluoride has been known, which Guntz [23] asserts he obtained as a bronze crystalline powder on introduction of very finely divided silver into a saturated solution of AgF.

As for the subchloride of silver, Ag_2Cl, Guntz considered it produced by the interaction of Ag_2F with tri-chloride of phosphorus at 140°. Vogel [24] used another method, allowing cuprous salts to react with silver nitrate. After drying, the resultant precipitate showed that its composition really corresponds to the formula Ag_4Cl_2 or Ag_2Cl. E. Baur[25] investigated thoroughly the formation of the alleged subchloride through action of fresh chlorine water on molecular silver. The vari-colored products resulting from the action of organic reducing agents have been especially studied by Carey Lea.[26] It was he [27] who gave the name *photo*halides to the multicolored mixtures formed by the action of light on silver chloride, which mixtures were supposed to consist of subhalides with AgCl.

E. Baur was the first to show that in dealing with the photohalides and the other subchlorides formed by the same procedure, we have no chemical individuals, but a continuous group of homogeneous mixtures ranging from metallic silver to pure silver chloride. The photobromide Ag_2Br of Carey Lea shows in a manner analogous to the photochloride Ag_2Cl, all transitions of color from a saturated lilac to deep violet.

3. Solubility of Metals in Salt-Melts

Many observations on the phenomenon of metal-fog suggest that there exists, even though to a small extent, a true solubility of metals in molten salts.

In order to determine the actual solubility, Lorenz and Helfenstein [28] proceeded to remove the previously weighed metal regulus from the melt, carrying on the operation at a given temperature. Experiments showed each time a considerable loss of weight in the regulus, increasing as the temperature rose, as for example, with lead in a lead chloride melt. The oxidation of metallic vapor at the surface of the melt forms lead oxide, which dissolves in the molten lead chloride.[29] This process naturally continually decreases the weight of the regulus submerged in the melt. As a result of this process, the greater the surface of the salt-melt exposed to the air, the greater the loss of weight of the lead regulus. Therefore, in determining the solubility, it is necessary as far as possible to limit this process, which is similar throughout to a process of diffusion of the metallic vapor through the melt. At the same

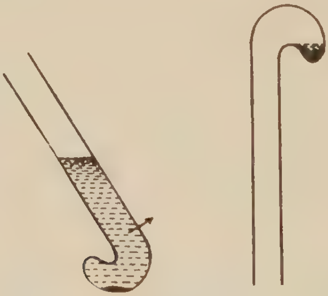

Fig. 1.

time it must be taken into consideration that on cooling the melt a considerable portion of the vapor condenses again. Therefore one cannot attempt to ascertain the solubility by separating the regulus from the melt after cooling, but rather by effecting a separation while the melt is in a liquid state. In addition Lorenz and Helfenstein [30] made use of the device shown in Fig. 1.

It is proven satisfactorily that the solubility of metals in molten salts increases with a rise in temperature. The amount of cadmium fog in a melt of $CdCl_2$ is relatively large. Thus cadmium vapors may be seen to arise from the electrolyte and deposit themselves in macroscopically visible droplets on the glass walls of the vessel holding the melt. To determine the metal concentration in the halide melts containing the vapor the following method may be pursued. As R. Lorenz, G. v. Hevesy, and E. Wolff observed, a phenomenon completely analogous to metal-fog occurs in halide melts if chemical reduction takes place, by introduction into the halide of a strong reducing agent, *e.g.*, potassium cyanide. Vice versa, on introduction of an oxidizing agent one can completely destroy the metal-fog present in the liquid melt. In the case of lead-fog in lead chloride, this takes place spontaneously when there is an excess of lead dioxide, according to the formula

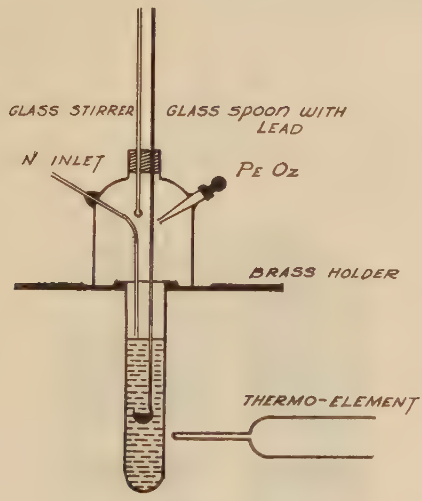

FIG. 2.

$$PbO_2 + Pb \rightleftarrows 2PbO$$

The lead oxide formed dissolves in the lead chloride melt. If lead chloride containing weighed traces of lead dioxide is added to a lead chloride melt containing metal-fog, the melt is instantly decolorized, due to the formation of more molten lead chloride and lead oxide which dissolves. In this way the determination can be carried out with great accuracy up to $\frac{1}{1000}$ of 1 per cent. The apparatus used is reproduced in Fig. 2. To it belongs an electric resistance furnace in the form of a cross (Fig. 3), which makes it possible to see through the vessel containing the melt. The following table shows the solubilities of lead in lead chloride:

Temp.	Solubility
550° C.	1.54×10^{-4}%
610	3.74 "
615	4.10 "
670	7.46 "

The repression of metal-fog through excess of alkaline chlorides, which Lorenz and Appelberg studied, could be determined quantitatively by the above described procedure. The following results were established, as expressed in Table I:

TABLE I

Solubility of Lead in Mixtures of Lead Chloride and Potassium Chloride

($PbCl_2 + KCl$)

The temperature of the melts is 610° C.

Mol. % PbCl	Mol. % KCl	Solubility
100	0	3.74×10^{-4}%
90	10	2.27 "
80	20	1.51 "
70	30	0.64 "
60	40	0.06 "

These observations are of exceptional technical importance for the electrolysis of liquid melts. (See below.)

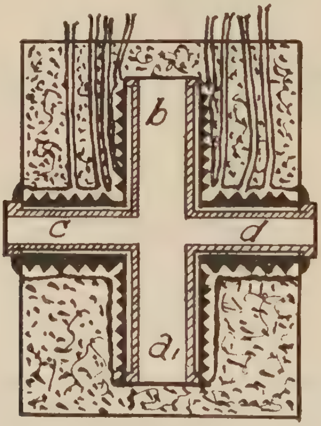

FIG. 3.

They prove that the masses of metal which produce the intense colorations of metal-fog are very tiny. This corresponds perfectly to the findings on colloidal metals in aqueous dispersion. The analogy seems very far-reaching. If one removes the lead cations from a lead chloride melt by transforming them into complex anions, to exactly the same extent is the formation of metal-fog (pyrosols) repressed. Lorenz and Fausti[31] as well as Lorenz and Ruckstuhl[32] in transformation experiments on $PbCl_2$-KCl melts, found that for lead complexes, formation increases in the direction of pure KCl. Fog-formation ceases completely when the melt contains 2 Mol $PbCl_2$ to 1 Mol KCl. This, however, corresponds to the double salt $KCl.2PbCl_2$ found through thermoanalysis, which has the anion $(Pb_2Cl_5)^-$. It seems that these same secondary valences, which are involved in the formation of the complex salt, are active in the formation of pyrosols. Therefore it is in order to regard the pyrosol or metal-fog as a fixation of lead in lead chloride.[33] We can describe it approximately by the formula $(Pb)_n.PbCl_2$. As a consequence metal-fog may be considered as an adsorption product of metal by molten salt, which breaks down more or less into metal and salt.

4. CONNECTION WITH VAPOR PRESSURE AND SURFACE TENSION

The formation of metal-fog is more intense the greater the vapor pressure of the metal at the temperature of the experiment. Also the softness of the metal seems to have a certain influence. An electric dispersion of the metal by the current of the metal, as people have called it, plays no part in the formation of metal-fog, since this takes place without electrolysis at the surface of the molten metal in the molten salt. The higher the boiling point of a metal, the greater is the range between appreciable vapor tension and the boiling point; and it is of practical significance that in many cases electrolytic separation takes place actually within this range of temperature. In the case of $PbCl_2$, which is liquid in the range between 506° and 956°, the metallic lead which separates during electrolysis forms at about 300° to 400° below the boiling point, in the region of a low but already perceptible vapor pressure. The losses of current on account of the formation of metal-fog are, at this stage, not yet significant. The current efficiency in the electrolysis of silver halides is excellent because of the high boiling point of silver. On the contrary in the electrolysis of $CdCl_2$ the loss of current from formation of metal-fog is extraordinarily large on account of the low boiling point of metallic cadmium (775°). If we electrolyze molten cadmium chloride at the temperature of boiling cadmium, the metal separates as a vapor, whereby only fog is found and no trace of regulus metal.

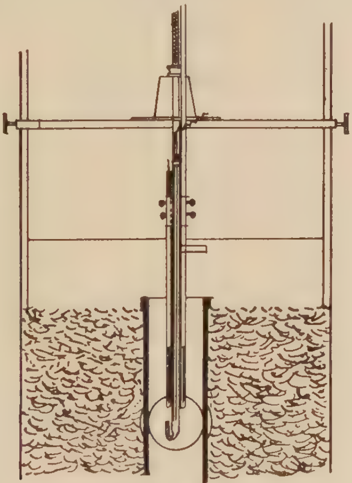

FIG. 4.

The hypothesis of the dispersoid nature of metal-fog leads immediately to the conclusion that a relationship exists between these phenomena and the surface tension at the interface between metallic regulus and molten salts. Such a connection was first found by Lorenz and G. von Hevesy.[34]

As already mentioned, the formation of metal-fog is influenced by additions of foreign salts to salt melts, in which the metal disperses. The surface tension between the metal and the salt is changed by such additions. Lorenz in collaboration with H. Frei[35] carried out elaborate investigations on the repression of metal-fog through additions. As a criterion the current efficiency during electrolysis was utilized. The formation of metal-fog decreases as the concentration of the additions increases, and is almost proportional to the molecular weight of the added salts. The quantitative determination of the surface tension between the metal and molten salt was carried out by Lorenz and Liebmann,[36] who used the method of the rise in capillary tubes. Liebmann's measurements of the surface tension between molten lead and molten lead chloride and its mixtures with KCl, have proved without doubt the correctness of the earlier observations and conclusions of Lorenz and Hevesy. It seems, therefore, that the surface tension works in opposition to the inner forces causing the formation of pyrosols, such as solution pressure, vapor pressure, etc. It thus follows that in the case of pure metals and those pure salts, where the surface tension is the smallest, the forces tending to form metal-fog are greatest.

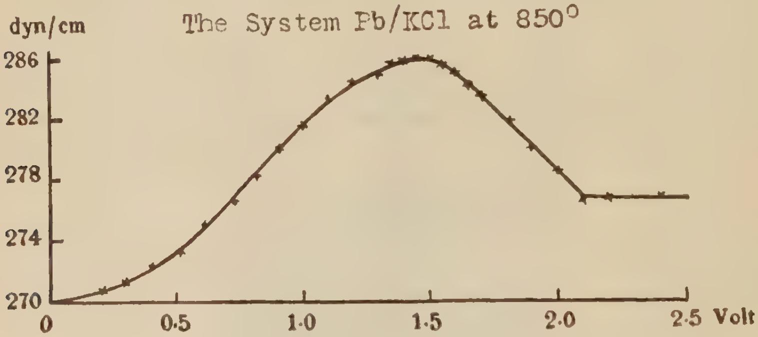

FIG. 5.

The above mentioned investigations of G. von Hevesy and R. Lorenz[37] on the electro-capillary phenomenon in molten systems are interesting. The system $Pb/PbCl_2$ in its molten state shows no change in surface tension as a result of polarization, and neither does the combination containing 50 per cent KCl. An increase in the surface tension with beginning polarization at the cathode is first to be seen in systems with less than 40 per cent $PbCl_2$. The system $Pb/PbCl_2$ does not polarize.

The system Pb/KCl behaves like an aqueous capillary-electrometer, as do all combinations of precious or semi-precious metals and the salts of a common metal. There is no fundamental difference between the electro-capillary phenomenon of melts and the aqueous solutions of electrolytes.

Fig. 4 represents the capillary electrometer of Lorenz and Hevesy, and in Fig. 5 the electro-capillary curve of the system Pb/KCl at 850° is reproduced from their experiments.

5. ELECTRICAL CONDUCTIVITY OF METAL-SALT SYSTEMS

A. H. W. Aten[38] undertook to investigate how solutions of metals in salts behave toward an electric current—whether they were of molecular or colloidal character—and to see what conclusions could be drawn from this behavior, as to the nature of this "solution." Using Lorenz and Kalmus' [39] method in solutions of Bi in $BiCl_3$ it was proved that with increasing amounts of Bi the conductivity of the system was correspondingly lowered. The decrease in the conductivity of $BiCl_3$ after addition of Bi could be connected, as Aten correctly points out, with the increase of viscosity produced by this addition.

Study of the system Cd-$CdCl_2$ furnished corroboratory results: the conductivity of this salt is also decreased by additions of the metal. On the basis of a functional connection of molecular conductivity with the formation of a binary salt mixture, which last Aten applies with reference to the metal-salt system, he concludes that the conductivity of the dissolved metal must be very much less than that of $CdCl_2$ and incomparably smaller than that of the compact metal.

Aten makes the interesting statement that it is most unlikely that CdCl (subchloride) exists as a stable compound, as was the contention of Morse and Jones. The possibility of the formation of the subchloride CdCl in the melt, however, must be either discarded or proven.

6. Technical Significance of the Pyrosols

Pyrosols, as previously indicated, possess great technical interest because they form in the electrolytes during electrolysis of melted salts and thereby disturb the mechanism of the current efficiency.

The metal-fog investigations of R. Lorenz and his students have thrown new light on the existence of cathode current losses to such an extent that they have finally cleared up the problem of the convection current.[40] If the metal separating at the cathode dissolves in the electrolyte in the form of a colloidal "fog," and if this fog reaches the region of the anode by means of a mechanical and thermal rotatory motion of the melt, the metal there will be instantly reconverted into its higher form of combination and will return to the cycle to repeat the process. This process forms a source of continuous disturbance which must inevitably lead to extremely great losses of current and considerable deviations from Faraday's Law. Thus the metal-fog acts as a typical depolarizer in the electrolysis of molten salts.

Lorenz and a number of students endeavored to test the conditions under which the electrolysis of the liquid melts of heavy metals halides may be so conducted as to fulfil the requirements of Faraday's Law, and repress the convection currents. His first experiments with A. Helfenstein [41] proposed to prevent the "diffusion" of electrolytes by working with a bath-temperature as near the melting point as possible. By way of example, the following results were obtained from the electrolysis of $PbCl_2$ showing the separation of Pb at the cathode. A V-shaped tube was used.

	Current yield in per cent		
t in °C	0.5 Amp.	1.0 Amp.	3.0 Amp.
540	87.7	92.1	97.3
600	80.1	87.7	96.4
700	66.7	76.6	92.0
800	42.4	54.9	72.6
850	7.0	...	...
900	...	12.3	44.4
920	...	3.2	...
956 (boiling point)	...	...	0

Fig. 6 illustrates the results of such experiments.

It was especially important to separate the electrodes, which was done by placing anode and cathode respectively in similar tubes or capsules made of potassium glass. Fig. 7 shows such an apparatus and in Fig. 8 the difference made in the current yield is plainly seen. The anode was immersed in the bath to a depth of only a few centimeters. With successive incapsulation of the electrodes there is a corresponding increase in the current yield, and the incapsulation of the cathode is especially important. In both cases ($PbCl_2$, $PbBr_2$, etc.) the theoretical figure corresponding to Faraday's law was reached. The best result obtained in this way was a current yield of 99.94 per cent in separating Pb from $PbCl_2$ with a current of one ampere at a temperature of 480° C., which proves that Faraday's Law applies fully in this case. The correctness of this law was also proved in separating silver from molten AgCl by the same method, at temperatures up to 1050° C.

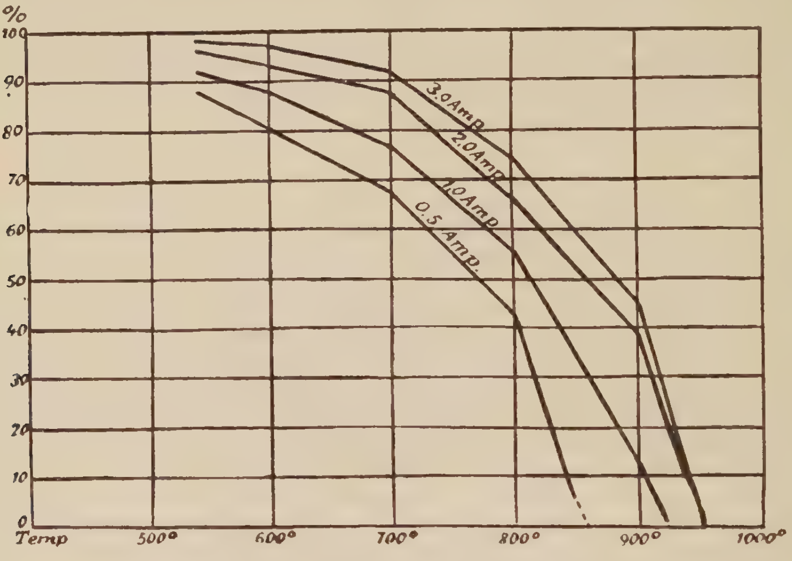

FIG. 6.—Chloride of lead. Influence of temperature.

A highly practical fact was discovered by Lorenz and Appelberg, namely that additions, as for example, of alkali chlorides to the liquid melts of heavy metal chlorides, almost completely repress the formation of metal-fog, and with it the convection-current.

In an earlier part of this paper we mentioned the influence of additions to molten electrolytes to change the surface tension at the face of the metal, and it is enough to call attention again to this connection which is so interesting from a scientific point of view. The difference in the current yield with and without addition of, for example KCl to $PbCl_2$ is very considerable and is more striking with a small current than with a larger one.

7. DISPERSED SYSTEMS

Closely bound up with the analogy of metal-fog with gold and copper ruby glass, is its analogy with other colloid systems in fluid and solid and even crystalline media. In the phenomena exhibited by blue rock-salt and the crystallized materials colored by cathode and radioactive rays, there is a peculiar similarity to the formation of metal-fog, which is paralleled by the developing of the photographic plate.

The colorations of metal-fog also deserve special notice in comparison with the colloidally dispersed hydrosols and organosols of metals, as well as with vapors. For example, in this connection should be recalled the deep-blue which Bunsen and Kirchoff observed in the electrolysis of molten rubidium and caesium chlorides and which correspond to the deep bluish-green ethersols of these same metals reported by Th. Svedberg.[43]

Maxwell Garnett[44] holds that a dispersed system consisting of the tiniest metal spheres must exhibit the same color as the vapor of the metal. In this respect, the analogy between the coloration vapors and hydro- and organsols, and that of metal-fog, gives final proof of the colloidal nature of the metals in pyrosols.[45]

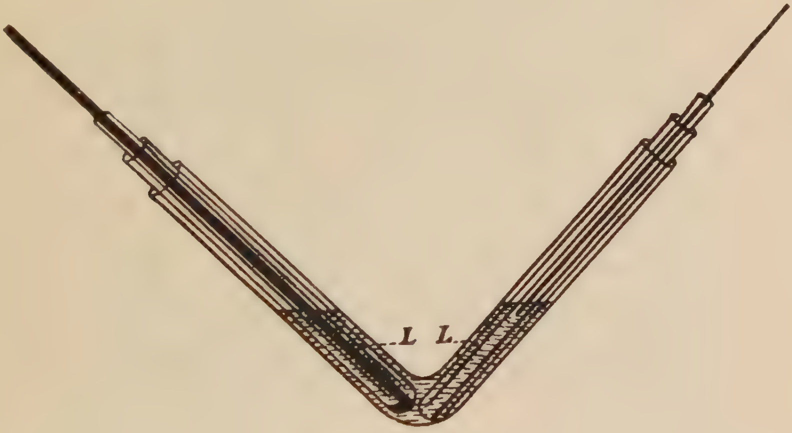

FIG. 7.

Ebell[46] made a special investigation of the formation of metallic copper during the technical manufacture of the various kinds of copper glass. By careful investigation he found that on sudden chilling, glass which contains metallic copper is *colorless*. Therefore the true metal solution must be colorless. As the glass was gradually warmed, the copper "condensed" into flakes from its saturated solution in the glass. In his work with glass colored by silver, Ebell proved an analogous condition.* R. Zsigmondy also studied silver-glass, and his experiments showed that the silver first goes into solution in the glass as oxide, but is reduced to the metal, and is finally found in the chilled glass in colloidal dispersion.

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* The fact that glass takes up silver from silver salts, was observed by R. Lorenz in numerous investigations. It was particularly referred to by Suchy (*Zeitschr. f. anorg. Chem.*, 27, 152 (1901)). A. Heydweiller (*Zeitschr. f. phys. Chem.*, **89**, 640 (1915)) says that the first bibliography is given by F. Kopfermann (*Dissertation*, Münster, 1908; see *Ann. d. Phys.*, 32, 746 (1910)). The action between silver salts and glass is a typical exchange reaction, like those which F. W. Clarke and W. Steiger investigated in the zeolites (analcim, chabalite, natrolith) with salts of heavy metals (see *Zeitschr. f. anorg. Chem.*, **46**, 189 (1905)). At high temperatures chlorides decompose and enter the silicate, forming silicon chloride and the noble metal. (See R. Lorenz, *Zeitschr. f. anorg. Chem.*, **31**, 385 (1902).) Furthermore, Lorenz and Helfenstein (*Zeitschr. f. anorg. Chem.*, **23**, 255 (1900)) observed that on electrolysis at 1050° molten silver chloride no longer yielded metal according to Faraday's law, because part of the silver was formed by the reducing action of the porcelain.

Undoubtedly metal-fog offers the most striking similarity to copper and silver-glass, as is especially well shown in the case of Cd fog in a $CdCl_2$ melt; the metal after hardening separates in the form of magnificent, very delicate, small crystals—just as in the Aventurine glasses. In both cases the presence of the pure metal is unquestionable.

Finally Zsigmondy's investigation of gold ruby-glass are particularly important. Ruby-glass behaves analogously to aqueous colloidal gold solutions. (Cf. Zeitschr. f. Electrochem. 4, 1898, 546.)

Gold ruby-glass, which is obtained by melting lead or barium glass with addition of a trace of gold chloride, is seen in the ultramicroscope to contain, like aqueous colloidal gold solutions, an enormous number of tiny gold particles.[47] The weight of gold necessary to produce a deep ruby color in the glass is extremely small; for example, one cubic millimeter of gold ruby-glass contains only about one eighty millionth of a milligram of gold. Zsigmondy and Siedentopf were able to show that there are some billions of gold particles in one cubic millimeter, after they had counted very small volumes by means of the ultramicroscope. The weight of the particles is of the order of 10^{-15} mg., and their diameter from 4 to 30 $\mu\mu$ (1 $\mu\mu$ equals 1×10^{-6} mm.). There are gold ruby glasses and gold sols with particles still smaller than these, which cannot be seen with the ultramicroscope. They appear optically empty and colorless, and may be regarded as homogeneous solutions of the gold in the glass.

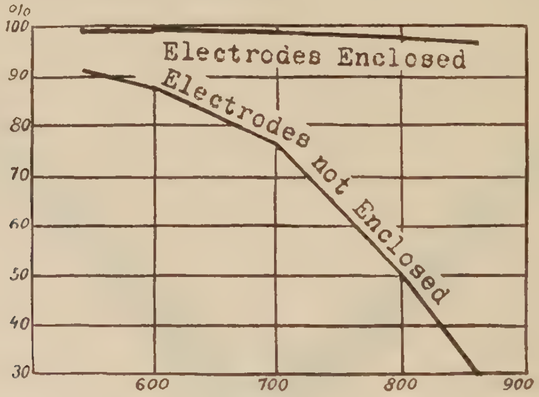

Fig. 8.

The "dissolved" metal-fog corresponds to the colored or colorless ruby glasses last mentioned. The usual metal-fog, as observed in the system Cd-$CdCl_2$, seems to contain a rather coarse dispersion. Zinc particles in $ZnCl_2$ are especially large. Between these extremes there undoubtedly exist all gradations, as in the metal-containing glasses.

In this connection we find of interest the experiments on borax-glass containing gold particles as recently carried out by A. Ehringhaus and R. Wintgen.[48] The metal could be observed in graded ultramicroscopic sizes. Ultramicroscopic count showed that the number of particles in borax-glass decreases with increasing duration of heat. This decrease is in correspondence with M. v. Smoluchowski's[49] theory of the coagulation of colloidally dissolved particles, which up to this time could only be confirmed with hydrosols. This beautiful investigation simultaneously confirmed the assumption of J. Donau,[50] that borax beads containing the precious metal, owe their characteristic coloration to colloidal solutions of the metal in the melt. H. Siedentopf[51] examined blue rock-salt with an ultramicroscope and found that the presence of very tiny crystals of metallic sodium is responsible for the coloration. As a result of treatment with sodium vapor, rock-salt takes up very fine deposit of the metal, which shows all the qualities of those found in natural blue rock-salt. On the other hand, it is possible to produce in rock-salt by partial decomposition by means of cathode rays, radio-active rays, Roentgen rays, and ultra-violet light, subtractive colors, which by suitable "developing" at higher temperatures are quite similar to those in the natural blue substance. Most of the particles are seen in the ultramicroscope to shine with a rust-brown color, analogous to the rust-brown gold particles which give its blue color to so-called sapphire glass, and correspond to what is most frequently met in natural and artificial rock-salt. The places which are deeply stained by Na vapor show distinctly the phenomenon of pseudo-pleochroism or phosphorescence which is peculiar to blue sapphire glass and yellow silver-glass.

Originally there were two opinions as to the nature of the changes which the alkali halides undergo during treatment with cathode rays, an observation of Goldstein.[52] Goldstein himself regarded the colorations as purely physical, but Wiedemann and Schmidt[53] supported the subhalide theory. R. Abegg[54] had tried very hard but without success to detect directly the small amount of halogen that was to be expected from decomposition of the salts. Therefore, Abegg came to the conclusion that chemical decomposition would not lead to the formation of subchlorides. F. Giesel[55] was the first to assume that the free alkali metal could be the coloring principle. By melting alkali metal together with salts he obtained, in fact, the same colors that are obtained by treating salts with cathode rays. The whole question, after Giesel's important preliminaries, followed by those of Siedentopf, was finally concluded in favor of the theory of colloidal dispersion of metals, in accordance with the facts which Zsigmondy and Lorenz had developed concerning the nature of pyrosols, each in his own field of research.[56]

In the same class fall also the numerous observations on the color change of minerals, especially those of the rock-salt group, which C. Doelter has made in the course of manifold experiments.[57]

Recently the experiments of K. Przibram and Marie Belar[58] have proved very productive. They worked on the color change of NaCl by Becquerel rays. Ultramicroscopic investigation of rock-salt crystals naturally and artificially colored, especially in their behavior toward heat (determination of the temperature of discoloration and its thermal luminosity) and change of the coefficient of absorption, proved the complete correspondence between the behavior of originally colorless salt and the natural violet salts, when the former had been colored golden brown by radium rays, and then had been turned violet by consequent heating to 200°. The discoloration temperature for both violet salts is between 200-250°. The natural blue salt found at Stassfurt is somewhat more stable. Salt colored by Na vapor (H. Siedentopf) is just as slightly thermo-luminescent as the colorless, while the natural blue and violet salts as well as those colored by radioactive rays, possess thermo-luminescent properties.

Many blue fluorspars,[59] which in their natural condition in visible light show only blue phosphorescence or none at all, fluoresce with a beautiful red color when exposed to radium rays (momentary radio-photo-luminescence).

8. ULTRAMICROSCOPIC STUDY OF METAL-FOG

Following a suggestion of Bredig,[60] in 1901 R. Lorenz and G. Auerbach [61] had already attempted to examine a solution of Cd in molten $CdCl_2$ according to Tyndall's principle, that is, to test whether the light scattered by passing a powerful beam of light through the melt is polarized or not. Testing for elliptical polarization was done by the method employed in optics.[62] In the system $CdCl_2$ no change in brightness could be distinguished. This tends to show that the light reflected from the metallic particles is natural or unpolarized light.

More recent investigations of Lorenz and Eitel [63] proved the dispersed condition of the metal-salt hardened with metal-fog. First, a pure, optically empty $PbCl_2$[64] was prepared, which as a result of treatment with pure $PbCl_2$ in a liquid melt with a stream of hydrochloric acid gas and chlorine, was freed from every trace of contamination. If we treat the melts of such very pure $PbCl_2$ crystals at 100-150° above the melting point (for about five minutes) with some pure bright metallic Pb, bright gray crystals are immediately formed. The lead chloride hardened with lead-fog shows under the ultramicroscope, as in the case of ruby-glass, countless shining points of light on a deep black background, which indicates the presence of a finely divided substance in the crystals. Every diffraction disc shows double as a result of the strong double diffraction of the $PbCl_2$, and the colored diffraction rings lying concentrically about the particles also show the same doubling. The method which Lorenz and Eitel used in the ultramicroscopic examination of such preparations, is shown in Figs. 9 and 10. The light emitted from the diffraction discs is completely linearly polarized. It is quite easy, with the help of such ultramicroscopic pictures, to recognize a definite arrangement of the particles of lead-fog in the $PbCl_2$ crystal aggregate, orientations of definite crystal surfaces

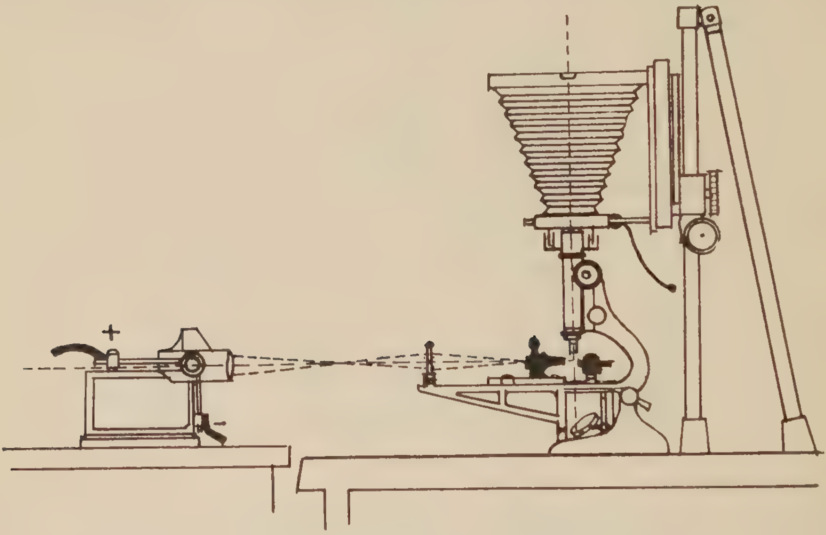

FIG. 9.—Ultramicroscopic apparatus for examination of metal-fog in crystals.

in twin crystals.* The metal-fog formed chemically by addition of traces of pure cyanide of potassium to optically empty $PbCl_2$, shows the same results. In this way we can produce a fog from a concentration of particles, from which it could not be otherwise obtained. Such melts are then a very deep black color and opaque. However, by treatment with chlorine and hydrochloric acid gas, they can be converted into the pure and optically empty chloride. The ultramicroscope is an extraordinarily sensitive instrument for detecting small fog-particles. A single melting and hardening of pure optically empty chloride is sufficient to make the particles reappear in circles of light. All these observations support the theory suggested by Lorenz,[65] that in molten metal halides a dissociation constant exists, which can be expressed by the rmula.

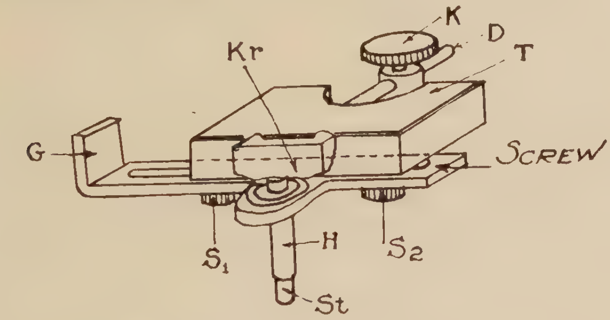

FIG. 10.—Apparatus for examining crystals of salts for metal-fog.

$$nMCl_2 \rightleftarrows \underbrace{(n-1)MCl_2 + M + Cl_2}_{\text{foggy melt}}$$

Lorenz and Eitel[66] extended their common investigation on the ultramicroscopic nature of the haloid melts containing metal-fog, to thallium salts, in which the formation of fog had already accidentally been observed in earlier investigations. The thallous halides differ from $PbCl_2$ in that when they have once been befogged they cannot be regenerated, since on treatment of their melts with free halogen, thallic halides are formed. The beclouding of the thallous halides was accomplished most simply by electrolysis. In strong transmitted light these melts show a deep brown color: the hardened masses of crystals appear brown and contain an enormous number of tiny particles, as can be seen with the ultramicroscope. But it is also possible to obtain befogged preparations by treatment of thallous salts with metallic thallium. A splendid orientation of the smallest ultramicrons, as in the octahedral surface of the regular crystals, is characteristic of thallium salts. As in the system Pb-$PbCl_2$, we can expect a reaction to take place in the molten system Tl-$TlCl_2$ in the direction that the thallous chloride becomes dissociated by the heat and the resulting free metal remains in the melt in the form of fog.

The analogous behavior of silver-fog in silver chloride and silver bromide melts is very important. R. Lorenz and A. Helfenstein[67] observed that the formation of silver-fog in molten silver chloride does not appear till the metal is melted and the temperature of the melt is considerably higher than the melting point of silver. Very pure, optically empty preparations of silver chloride and silver bromide are restored by treatment of the melt with chlorine and HCl, or Br and HBr. Befogging is easily accomplished by addition of pure silver at 1100°. Misty crystals then show (in the ultramicroscope) extraordinarily finely dispersed silver particles, a condition which completely corresponds to that in gold ruby glass.

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* For ultramicrophotographs see *Zeit. für anorg. Chemie,* 91 (1915).

Since in the optical examination of silver halides, these latter are penetrated by a very intense light, it is of interest to observe their behavior after prolonged exposure. Optically empty preparations remain practically unchanged, but one notices that they gradually become less transparent, and are discolored to violet or black, quite similarly to photographic paper sensitized with AgCl. A Tyndall cone was not observed by Lorenz and Eitel during their exposure.

9. The Silver Germ Theory of the Latent Photographic Image

The phenomenon of metal-fog, arising when metals are brought into contact with molten salts, may be applied to the explanation of the latent photographic image, for upon exposing a photographic plate there is formed a solid solution of metallic silver in silver bromide, which initially contains particles merely submicroscopic in size, but nevertheless capable of forming the first silver nuclei.

As far back as 1897, R. Abegg[69] advanced the view that in the exposed photographic plate the presence of metallic silver must be inferred, and that the effect of these silver germs or nuclei upon the development of the impression made by the light, closely resembled the removal of supersaturation in solutions by crystal nuclei.[70] However, he relinquished this view in favor of the photo-haloid theory which was then developing. Richard Lorenz[71] in 1900 adopted it independently of Abegg, and showed the similarity between the latent photographic image and the metal-fog he had made.

This theory of Abegg and Lorenz superseded the older one, according to which exposure of the silver halides was supposed to give rise to subhalides, as was maintained by Eder and Vogel, and supposedly proven by them experimentally. Abegg took the stand that, with the exception of Ag_2F,[72] the silver subhalides were mixtures of silver halide with metallic silver. Upon bathing exposed plates in dilute nitric acid, the light effect capable of development vanished almost quantitatively. Even as far back as 1810, Eder observed that an unexposed plate when placed in a developer, developed at such points as it had been in contact with a silver wire. Further, the picture in a finished negative could be intensified by layering over it unexposed emulsion, and then developing again.[73]

According to Guebhardt[74] the sensitiveness of rapid plates is due to the fact that, prior to exposure, they are coated with a thin layer of silver germs formed by the slight reducing action of the gelatin on the emulsion in question. The developability of a plate fixed immediately after exposure is also readily explained by the silver germ theory. On the basis of this phenomenon, L. and A. Lumière and A. Seyewetz[75] recently based a valuable method of germless development of photographic images. This important observation is remarkable because of the necessity of having an organic developer in the developing bath, which they try to explain on the basis of the subhalide theory as being due to a kind of modification of the "subbromide." The silver grain in this process is a simple crystal. Addition of molecular silver in fine subdivision increases the developability of the plate.[76] From all this Abegg concluded that the assumption of subhalide formation by exposure was improbable, but that all the phenomena could be simply explained by the view that the light produced silver nuclei. The question then arises as to the state of the metallic silver present. Upon discovering metal-fog, Lorenz immediately saw the striking analogy and espoused the silver germ theory, which in his opinion had thus received a reasonable and sure foundation.

At present this state of the question is illustrated by the analogy between gold sols, and ruby-glass and metal-fog. The work of Lorenz and Hiege (see below) should finally settle the matter. On the other hand the sub-halide theory met serious difficulties [77] when the products of exposure were compared with those obtained by Guntz and Vogel. Furthermore, the experiments of E. Baur [78] on the action of chlorine water on colloidal silver, showed that the substances obtained, which corresponded to Carey Lea's photo-haloids,[79] constituted a series of solid solutions.

If we imagine that in a silver sol there is partial formation of silver chloride, the silver particles would be at once condensed on the surface of this chloride. Van Bemmelen has shown in other systems that there are "adsorption compounds" which do not follow stoichiometric laws, but are due to adsorption or agglutination in indefinite proportions. Photochlorides may be such compounds, *i.e.*, colloidal silver and AgCl. They may be formed in aqueous solutions as well as in fluid melts (pyrosols). This is certainly the case with the suspension of zinc dust obtained by metal-fog formation in a melt of zinc chloride containing water, for here the zinc fog condenses on colloidal zinc hydroxide formed by electrolysis in the melt.[80] The photochlorides may also be compared with the purple of Cassius investigated by R. Zsigmondy,[81] which, despite the fact that it is a mixture of colloidal gold and colloidal stannic acid, behaves like an individual substance. In such substances the properties of one ingredient may be masked by those of the other, so that it would seem as if we had a new substance which behaved differently from its constituents, a new chemical compound having special properties. Since this was the case to a marked degree in the photo-halides, it was assumed that they were definite compounds with different properties from their components, silver and silver halide.

The adherents of the sub-halide theory [82] argued that, if photohalides were mixtures of metallic silver with silver halide, then nitric acid should be able completely to extract the former (which Eder was unable to do); and an exposed plate, after bathing in nitric acid, could nevertheless be developed. On the other hand the work of Lorenz brought out a whole series of facts regarding the behavior of colloid mixtures. The profound studies of Lüppo-Cramer on this subject [83] showed the unsoundness of objections to the view that the photo-halides behave anomalously. He was able to prove directly [81] that silver bromide could protect adsorbed silver so completely, that the silver could not be dissolved out by dilute nitric acid. If hydrosols of silver and silver bromide are mixed and concentrated nitric acid is immediately added, the silver is dissolved out, for no adsorption has yet occurred. If, however, a coagulation has first occurred (*e.g.*, by addition of H_2SO_4) the nitric acid can no longer extract the silver from the precipitate, which in color appears like a true photo-haloid.

The protective action of silver bromide on colloidal gold may also be demonstrated. Aqua regia cannot extract gold from an Au-AgBr coagulum. It is most interesting that gold nuclei, when mixed into silver bromide, facilitate the reduction process even in silver-reducing media, as was noted by H. Weisz,[85] and as was later proven by Thomae in Zsigmondy's laboratory. Thus gold nuclei when added to silver bromide, act just as if the latter were exposed or had silver nuclei added. This settled the question of the principle underlying the action of silver germs or nuclei in the latent image, and the subhalides or photo-haloids were recognized to be colloidal mixtures of silver with silver bromide.[86] That exposure must cause a superficial change in the grain of silver bromide, already has been shown by F. Kogelmann[87] in his beautiful though little known work. On the other hand the changes produced by solarization occur rather at the interior of the AgBr grain. That the silver grain produced on developing exposed AgBr must lie on the surface, was recently confirmed by J. Eggert and W. Noddack.[88]

Decisive evidence in favor of the colloid nature of the photo-haloids is given by the recent work of W. Reinders,[89] who first showed that at either high or at low temperatures, silver and silver chloride gave stable colored intermediate compounds, especially as there was no question of solubility of molten silver in silver chloride, apart from the silver-fog obtained, which at most was 0.1 per cent. The colored crystals had the same form as ordinary uncolored ones. In concentrated solutions of ammonia or sodium thiosulphate the crystallized photo-haloid yields a colorless solution of AgCl, with a residue of silver as a black powder, at most 0.5 to 1.0 per cent, but usually only 0.1 to 0.5 per cent. This careful investigation compels the belief that the photo-haloid obtained by exposing silver halide is an adsorption of silver and silver halide. Schaum and Lang,[90] in accord with the work of Reinders, showed that the color-producing particles of the photo-haloid are of a size corresponding to that of silver particles of 60 to 180 μμ, as was predicted by the optical theory of Mie.[91]

The complex nature of the latent photographic image is due to the fact that in emulsions of gelatin dry plates there is a complication of colloid-chemical phenomena with those of crystal growth. This is shown to no small degree by the work of Lüppo-Cramer[92] on the ripening of emulsions of AgBr, AgCl, AgI, and other salts. The growth of the particles follows a typical Ostwald ripening, *i.e.*, the intermediate solution of one portion with simultaneous increase in grain size of the rest, the larger particles growing at the expense of the smaller ones.[93] Lüppo-Cramer also proved that colloidal silver could undergo Ostwald ripening.[94] Silver iodide when exposed to light, forms a remarkable dust-like mass.[95] Furthermore, the phenomenon is noticeable even on exposure to X-rays,[96] and is obviously due to a profound decomposition of the silver bromide. It must be recalled that according to Lorenz the basic formula for the formation of the latent image is

$$n(\mathrm{AgBr}) + \text{Light} = \underbrace{(n-1)\mathrm{AgBr} + \mathrm{Ag}}_{\text{Latent Image}} + \mathrm{Br}$$

so that on exposure there is a liberation of halogen. Because of the volatility of the halogen, the space lattice at the illuminated places might readily be disturbed, and this could happen perhaps with explosive violence, whereby the formation of dust could easily occur.

R. Lorenz and K. Hiege[97] tried to discover whether they could observe ultramicroscopically the silver nuclei which, according to the theory of Abegg (and Lorenz), were formed on the exposure of silver halide. Lorenz and Eitel (*loc. cit.*) had found that on examining silver fog in silver chloride melts in the slit ultramicroscope, long illumination of homogeneous specimens developed a color; but they had been unable to see particles. If such particles separated, they must have been amicroscopic. But they were able to observe that the ultramicroscopic picture yielded by a fog-free silver halide crystal, is identical with that yielded by "fog-formation." This proves the connection with the latent photographic image.

Lorenz and Hiege proceeded differently from the earlier work of Lorenz and Eitel, in that they directed the light cone of the slit ultramicroscope directly on the surface and followed the changes there. After a short time there appeared a browning where the light impinged, and there developed a large number of very small and very bright points, whose size gradually increased. The particles thus developed were recognized as metallic silver. The initial browning was due to amicrons, which gradually grew to submicrons.

The silver germs formed by insolation may be also developed into large ultramicrons by heating for several hours in the dark to 350°. The silver germs produced by heating without insolation, by simple fog formation, were fainter and less numerous. The particles formed by insolation in a crystal of silver bromide originally optically clear, are capable of growing in the dark on warming, and evidently at the expense of their surroundings; this is quite like the gold particles observed by Zsigmondy.*

All these facts indicate that the action of light on a silver halide crystal causes a separation of metallic silver, and that the latent image is a typical dispersoid phenomenon. It is still to be determined whether the fog and particles observed by Lorenz and Hiege in insolated silver bromide, show in all respects the same chemical behavior as the latent image, *e.g.*, whether they react with sensitizers, etc.[98]

In order to avoid the complicated system of the gelatin dry plate, etc., as well as the disturbing influence of the intermediate medium of Lorenz and Hiege, W. Ehrlers and P. P. Koch [99] used single crystals without a binder in their work on the changes in mass of the silver bromide grain upon insolation with white light. They used the suspension condenser according to Ehrenhaft and Millikan,[100] † which enables one to measure directly the change in mass of a silver bromide grain under the influence of illumination. A continuation of this extremely interesting work by P. P. Koch and F. Schrader [101] with perfected apparatus, on grains of AgCl, AgBr and AgI, showed mass changes of 1 to 2 per cent at the most with an intensity of illumination of 3,000,000 to 12,000,000 meter candle seconds; and much weaker illumination (*e.g.*, 2300 meter candles for AgBr for 5 seconds), produces distinct coloring.

By use of a Salvion microbalance in high vacuum [102] was able to show that on intense illumination silver bromide grains suffered considerable loss in mass.

R. Schwartz and H. Stock,[103] as well as P. Gross,[104] attacked the question of loss of halogen from another angle. By measuring the halogen liberated by photochemical decomposition of the silver halide in layers having no binding material, they sought to prove that halogen liberation parallels blackening of the photographic emulsion, and further, that the sensitivity to light depends largely on the condition of the silver halide, especially on its age and the conditions of its formation. Considerable difference was shown among the various preparations of silver halides, according as they were formed in the presence of alkali halide, or in the presence of an excess of silver nitrate—

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* Consider also the growth of crystals at the cost of others consequent on surface forces, as pointed out by G. Tammann. This he attributed to a recrystallization process.

† For Millikan's falling drop method, see p. 177. J. A.

i.e., as brom or chlor substances, or as silver substances, in the sense of Fajans.[105] On insolation only the brom substance evolved bromine, while in the case of silver chloride, both the chlor and the silver substance evolved chlorine. The moisture present has marked effect on the accuracy of the determination of halogen, because of secondary reactions between the water and the halogen. Moist AgCl silver substance is more powerfully decomposed than dry, while there is little difference between moist and dry chlor substance. The intense coloration of the moist silver substance indicates its great sensitiveness, but on the other hand the dry chlor substance is certainly more strongly decomposed photochemically than silver substance, and especially remarkable is the very slight sensitiveness of dry AgBr silver substance. However, it is well known that silver substance is more light sensitive in the photographic sense, and all photographic emulsions are prepared as "silver substance" by using an excess of $AgNO_3$.

The conflict between photochemical and photographic light sensitiveness is, therefore, only an apparent one, and is due to the fact that the latter is measured by behavior on short insolation and subsequent development, and development is not a simple process, showing (according to Vogel) different results according to whether it is done in acid or in alkaline medium. Unquestionably AgBr is more sensitive to light than AgCl, but nevertheless AgCl colors up darker than AgBr. Photochemically, AgCl is more sensitive than silver substance. Curiously, AgCl produces no solation as compared with AgBr, for even with the highest intensity of light the Cl split off is directly proportional to log J, whereas with AgBr there is a recession of Br liberation at high intensities, which must be considered as analogous to solarisation.

The course of photochemical dissociation is also quite instructive; the curve obtained by plotting recurrent insolation at constant intensity against halogen evolved per unit of time, shows a maximum which is reached only after a certain photochemical inductive period.

As to ageing phenomena, fresh AgCl silver substance shows less photochemical decomposition than aged material, which is analogous to the ripening of silver halide emulsions.

All these observations furnish convincing proof of the correctness of Lorenz' theory of the latent image.

10. DISPERSOIDS OF THE MINERAL KINGDOM AND OF SLAGS

Lorenz and Eitel were the first to study under the ultramicroscope colloidal solutions of solid dispersoid phases in a solid dispersion medium. These hardened metal-fog preparations are typical of a large number of substances found in nature, especially those minerals which are allochromatically stained by the presence of finely divided pigment.

Pyrosols, which may be regarded as fluid-dispersoid systems in fluid media like emulsoids, are analogous to substances frequently found in nature, as for example, the obsidians, pitch-stones, and other glassy lava stones in which fluid particles of dispersed substances, frequently of ultramicroscopic size, are distributed. The pyrosols also correspond to certain artificial substances, such as the water-glass synthesized by Barus [106] and the sulfide silicate melts formed as steel slag which J. H. L. Vogt [107] investigated. A wide field is open for the investigation of the phenomenon of metal-fog, in view of the fact that emulsoids of the pyrosol type are in their solution phenomena similar to the homogeneous, complex fluids which show de-solution. It is possible to derive the solubility curve of a metal in the melt of its salts from the de-solution phenomena which appear during the cooling of the solution, if the latter is separated from the superfluous metal. One must determine at what temperature the solution becomes clear and at what temperature it becomes cloudy during cooling. The cloud would not be formed as a de-solution dispersoid by emulsing the metal at the surface between metal and salt, but it would be produced in the metallic salt solution itself. The separation of the fog, therefore, would be quite analogous to the de-solution process of the homogeneous fluid phases in the system Phenol-Water.[108] Especially in FeS, CoS, PbS, ZnS, Cu_2S, Ag_2S, the so-called "stones" * of metallurgic processes, we have, according to Vogt's studies, excellent examples of limited solubility and also examples of a series of de-solution dispersoids from those consisting of the smallest ultramicroscopic particles up to large particle suspensions. Iron sulfide is not found in crystallized form in such slags, but is suspended in highly dispersed particles in the obsidian-like opaque black glass. The larger aggregates may appear in the characteristic form of drops. The black glass, seeming optically quite homogeneous, gives the impression of an ultramicroscopically fine dispersion analogous to gold, silver, copper, and lead glass. As a supplement to his earlier observations, R. Lorenz recently published interesting studies on slags [109] containing manganese-fog. A splinter of this brown glass, peculiarly iridescent when the light strikes it, shows in the ultramicroscope a large number of very fine particles of golden-yellow brilliance, which recall those in gold ruby-glass. Analogously to the formation of the colloidal gold in the latter, the metal in this case originates from a reduction process in the manganese-glass. However, the manganese is appreciably volatile at the furnace temperature.[110] Therefore, it may have diffused directly from regulus metal into the glass in the form of a fog, in a manner similar to the formation of the fog in the systems Cd-$CdCl_2$, Pb-$PbCl_2$, etc.

Besides de-solution dispersoids of fluid partial phases from homogeneous fluid phases, there are also frequently found in nature de-solution dispersoids of crystallized substances from a homogeneous mixed crystal phase. They also show distinctly all transition points from suspensions of amicronic small particles up to a microscopically visible fog of large dispersed particles. We may here mention the innumerable inclusions in nephelin, the separation of iron oxide from feldspar, the separation of anorthite-microperthite, titaniferous magnetite, inclusions in hypersthine and labradorite, etc.[111]

By means of the ultramicroscope the de-solution processes of alkali halides were investigated, and W. Eitel [112] succeeded in following them step by step, especially in the system NaCl-KCl, under widely differing concentrations and under the most varied circumstances.

The high color intensity of metal-fog finds its parallel in many allochromatically colored minerals, for example, ruby, sapphire, fluorspar, rock-salt, soda-lithia minerals (in analogy with ultramarine), etc.

We may here refer to the detailed and extensive work of C. Doelter,[113] to the work of E. Weinschenk,[114] K. von Kraatz-Koschlau and L. Wöhler,[115] and many others.

We must always remember the point of view which C. Doelter advanced regarding the coloration of mineral salts and which has been known as a fact for a long time in connection with metallic hydrosols and pyrosols: Different colors (in this case, a mineral) are not necessarily caused by different pigments; one substance may show quite different colors on account of changed

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* Such substances are commonly called *sonims.* J. A.

size of the particles, and even the change of a colloidal system into a crystalline one may be observable as a change in coloration.* If radiation does play the main rôle in the origin of colloidal allochromatic pigment, by which colloidal metals produced by electrical dispersion enter the substance—this question will probably be solved analogously to those of metal-fog and pyrosols.

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* Thus ferric oxide has many colors, depending on mode of formation and treatment, and lead chromate may vary in shade from a bright lemon yellow to a deep orange. Mere change in particle size may suffice to produce color change, not necessarily an orientation in a crystal space lattice. Colloidal particles may be crystalline, and need not necessarily consist of random clusters of molecules. J. A.

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The Adsorption of Gases by Metals

By L. L. Bircumshaw, B.A., M.Sc.

A considerable amount of work has been done on the adsorption of gases by various substances, chiefly charcoal, but measurements of the adsorption of gases at metallic surfaces are comparatively rare. The problem of adsorption at plane crystalline surfaces has been attacked by Langmuir in three extremely important papers.[1, 2, 3] The fundamental idea involved is the extension of the Braggs' work on the structure of crystals to chemical processes at surfaces. Langmuir considers that the forces affecting adsorption may be due to the electromagnetic fields of force resulting from the residual affinity of the atoms on the surface of the solid. These may be the result of either primary or secondary valence, but he brings forward evidence that in a number of cases the union between the surface and the adsorbed film is the result of the strongest kind of chemical union (primary valence).

Langmuir considers that the orientation of the atoms on the surface of a crystal constitutes in effect a sort of "checker" board, and that when the molecules (or atoms) of a gas are adsorbed, this takes place by the filling up of certain definite "elementary spaces." These spaces may be of more than one kind. Thus in the arrangement of the hydrogen and oxygen atoms on the lattice of the following surface:

H O H H O H
H H O H H O
O H H O H H
H O H H O H
H H O H H O
O H H O H H

Considering the area of an elementary space as that covered by four atoms, then we may have two types of space viz.: $\genfrac{}{}{0pt}{}{HO}{HH}$ and $\genfrac{}{}{0pt}{}{HO}{OH}$, the adsorption of these spaces will differ, and this may cause the adsorption to take place in steps; or when different gases are alternately adsorbed, maximum surface adsorption will take place in stoichiometric proportions. It is important to notice that in Langmuir's theory, although the forces which give rise to adsorption are identical in nature with the forces operative in the formation of chemical compounds, yet the phenomenon is not due to the production of definite compounds such as certain earlier workers in this field have postulated.

Langmuir develops a formula[4] for the rate at which a gas comes in contact with a surface.

$$m = \sqrt{\frac{M}{2\pi RT}} \times p \qquad (1)$$

where m is the number of grams of gas striking a sq. cm. of the surface per second, M is the molecular weight, T is the absolute temperature, p is the pressure in bars,* and R is the gas constant $83.2 \times 10^6 \frac{\text{ergs}}{\text{deg.}}$. If μ is the number of gram molecules striking one sq. cm. of the surface per second, then

$$\mu = \frac{p}{\sqrt{2\pi MRT}} = 43.75 \times 10^{-6} \frac{p}{\sqrt{MT}} \qquad \text{(2) and (3)}$$

A certain fraction a of the molecules which strike the surface will condense before they evaporate off again, and it is considered that there is good evidence that a is very close to unity. It will be seen also that on this theory, adsorption is a direct consequence of the time lag which exists between the condensation and evaporation of molecules at the surface.

Consider a surface which has N_0 elementary spaces per sq. cm., then this is also the number of molecules (in a case of simple adsorption) required to form the adsorbed layer. The rate of evaporation from the second layer of the gas will be very much more rapid than from the first, in fact in many cases, it will amount to a reflection. If θ represents the fraction of the surface which is bare, $a\theta\mu$ gives the rate of condensation of the gas, and $\nu_1\theta_1$ represents the rate of evaporation, where θ_1 is the fraction of the surface which is covered and ν_1 the rate of evaporation if the surface were completely covered. For equilibrium at the surface we have

$$a\theta\mu = \nu_1\theta_1 \qquad (4)$$

also

$$\theta + \theta_1 = 1 \qquad (5)$$

whence

$$\theta_1 = \frac{a\mu}{\nu_1 + a\mu}. \qquad (6)$$

If we put

$$\frac{a}{\nu_1} = \sigma_1 \qquad (7)$$

then (6) becomes

$$\theta_1 = \frac{\sigma_1\mu}{1 + \sigma_1\mu} \qquad (8)$$

If η is the number of gm. mols. of gas adsorbed per unit area of surface, then:

$$\frac{N}{N_0}\eta = \theta_1 = \frac{\sigma_1\mu}{1 + \sigma_1\mu} \qquad (9)$$

This equation gives us the relation between the pressure of the gas which is proportional to μ, and η, the amount of gas adsorbed at the surface. Both of these are capable of experimental determination, so that N_0 and σ_1 can be calculated.

Langmuir has also derived formulæ for the case (1) when there are several kinds of elementary spaces representing fractions of the surface:

$$\beta_1 + \beta_2 + \beta_3 \ldots\ldots\ldots = 1$$

which can be written

$$\frac{N}{N_0}\eta = \frac{\beta_1\sigma_1\mu}{1 + \sigma_1\mu} + \frac{\beta_2\sigma_2\mu}{1 + \sigma_2\mu} + \qquad (10)$$

(2) adsorption at amorphous surfaces when the spaces *may* be all unlike:

$$\frac{N}{N_0}\eta = \int_0^1 \frac{\sigma\mu}{1 + \sigma\mu}\, d\beta \qquad (11)$$

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* 1 Bar = 10^{-6} Atmospheres.

Where σ is a function of β, *i.e.*, $d\beta$ is an infinitesimal fraction of the surface, each element having its corresponding value of σ. (3) When each elementary space can hold more than one adsorbed molecule:

$$\frac{N\eta}{N_0}=\frac{\sigma_1\mu+2\sigma_1\sigma_2\mu^2+3\sigma_1\sigma_2\sigma_3\mu^3+}{1+\sigma_1\mu+\sigma_1\sigma_2\mu^2+\sigma_1\sigma_2\sigma_3\mu^3+}. \tag{12}$$

Where, if θ represents the fraction of the spaces which contains no adsorbed molecules and θ_n the fraction of spaces which contains η molecules,

$$\begin{aligned} \text{then}\quad 1 &= \theta+\theta_1+\theta_2+\ldots\ldots\ldots\theta_n \\ \text{and}\quad \theta &= \theta_1/\sigma_1\mu \\ \theta_2 &= \sigma_2\mu\theta_1 \\ \theta_3 &= \sigma_2\sigma_3\mu^2\theta_1,\ \text{etc.} \end{aligned}$$

An important case is that of atomic adsorption, which for the case where the total adsorption covers only a small fraction of the surface, reduces to

$$\frac{2N\eta}{N_0}=\sqrt{\sigma\mu} \tag{13}$$

or the adsorption is proportional to the square root of the pressure (for the case where two elementary spaces are occupied by the atoms of the molecule).

Langmuir points out that the results obtained by a study of adsorption phenomena cannot be explained by any single formula. An examination of the data put forward by Freundlich shows that in his well known equation

$$q=ap^{\frac{1}{n}} \tag{14}$$

(where q = quantity of adsorbed gas; p = pressure; a = a constant; and n is a constant greater than unity), $\frac{1}{n}$ approaches unity for low pressures and high temperatures, but for high pressures or low temperatures $\frac{1}{n}$ may become as small as 0.1. This is easily explained on Langmuir's theory. If we turn to equation (9) we find that the term $\sigma_1\mu$ may be neglected in the denominator at low pressures or high temperatures. The gas adsorbed then varies as the pressure μ. At high pressures or low temperatures the adsorbed gas tends to a limiting value (saturation), and as this limit is approached, the value of $\frac{1}{n}$ in Freundlich's equation must gradually decrease. According to equation (9) q and p will be related by the equation

$$q=\frac{\text{abp}}{1+ap} \tag{15}$$

where a and b are constants related to σ_1, N_0, M, and T. This can be rewritten,

$$\frac{p}{q}=\frac{1}{ab}+\frac{p}{b} \tag{16}$$

and by plotting $\frac{p}{q}$ as a function of p the constants a and b were determined. Using these values q cal. was compared with q obs. from his experimental data.

Langmuir then calculated N_0 from his experimental data in order to see if these values corresponded to an adsorbed layer not exceeding one molecule in thickness.

Dividing equation (15) by b and comparing it with (9), we get:

$$\sigma\mu = ap$$

and

$$N_0 q = bN\eta \tag{17}$$

q being expressed in cu-mms. of gas and absorbed on the surface s, and η being the corresponding number of molecules per sq. cm. Now one cu. mm. of gas at 20° and 760 mm. pressure is 4.16×10^{-8} mols. and we get:

$$\eta = 4.16 \times 10^{-8}\, q/s.$$

Substituting this in (17) and putting $N = 6.06 \times 10^{23}$, we have $N_0 = 25.2 \times 10^{15}\, b/s$, from which equation N_0 can be directly calculated.

Now if we take the average distance between the atoms of solids as 3×10^{-8}, then the area covered by each is 9×10^{-16}, and the number of atoms per sq. cm. is of the order of 10^{15}. This order of magnitude is in agreement with the values of N_0 found. The number of molecules required to form a monomolecular layer was calculated from the molecular volume of the adsorbed substance in the liquid state. For nitrogen the number per sq. cm. is 0.66×10^{15}, for methane 0.63×10^{15}, for carbon monoxide 0.66×10^{15}, for argon and oxygen 0.77×10^{15}, and for carbon dioxide 0.61×10^{15}.

Langmuir studied the adsorption of various gases, and in the case of glass and mica found that the adsorption at room temperatures was negligible. In these cases also at lower temperatures (90° K. and 155° K.),* he found that the observed values of N_0 were considerably less than the calculated values, showing that the amounts of gas required to saturate the surface under these conditions were always less than the amounts required to form a monomolecular layer, from which he concluded that the adsorption of most of these gases did not occur over the whole surface, but only in a region where the stray fields of force of the atoms were particularly strong.

In the experiments on platinum, the metal used was in the form of foil 15.3 × 10.2 cms. and a thickness of 0.0010 mm. The weight was 4.03 gms. and the total surface 312 sq. cms. The first tests, which were made with hydrogen, oxygen, and carbon monoxide, showed practically no adsorption at room temperatures, and also when cooled in liquid air, but after the metal had been heated to 250° in a mixture of hydrogen and oxygen (neither gas alone would activate the platinum), adsorption of both oxygen and carbon monoxide was noticed. Thus, if oxygen and carbon monoxide were introduced, one of these gases being in excess, then an abnormal disappearance of the gas in excess was observed; and if a mixture was then used containing the other gas in excess, an abnormal disappearance of part of the excess of gas would be noticed. These results could be explained by the supposition that the gas added in excess becomes adsorbed on the metal, and subsequently reacts with the other gas when brought in contact with it. The results obtained by the alternate treatment of the metal with oxygen and carbon monoxide are shown in full in the table.

To arrive at an estimate of the gas adsorbed in this way it was necessary to determine the amount of carbon dioxide formed. This was done in the series of runs given in the following Table (I), and from these results the amounts of gas absorbed by the platinum (not removed by exhausting), were calculated (Table II).

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* The pressure in these experiments varied from 1 to 170 bars.

TABLE I

TREATMENT OF PLATINUM ALTERNATELY WITH OXYGEN AND CARBON MONOXIDE

Run	Gas	Temp.	Initial Amount Cu. Mm.	Contraction Cu. Mm.	CO_2 Formed Cu. Mm.	Adsorbed O_2	Adsorbed CO	Loss of O_2	Loss of CO
1	CO	200°	35.9	15.6	11.2	5.6	4.4		0.5
2	O_2	200°	30.6	8.5	3.9	6.6	3.9	1.4	
3	CO	200°	25.0	14.8	10.6	5.2	4.3		0.4
4	O_2	330°	29.0	12.7	3.9	10.8	3.9	5.6	
5	CO	330°	29.9	13.4	10.5	5.2	2.9		1.7
6	O_2	330°	29.6	8.9	1.2	8.3	1.2	4.7	
7	CO	100°	28.4	11.5	7.3	3.6	4.2		0.1
8	O_2	100°	27.4	5.6	4.1	3.5	4.1	—0.1	
9	CO	100°	26.6	11.4	7.3	3.6	4.1		0.5
10	O_2	20°	26.6	4.5	3.6	2.7	3.6	0.6	
11	CO	20°	27.8	8.5	4.2	2.1	4.3		0.8
12	O_2	20°	29.0	4.5	3.5	2.8	3.5		

TABLE II

AMOUNTS OF OXYGEN AND CARBON MONOXIDE ADSORBED BY PLATINUM

Temp.	Oxygen Cu. Mm.	No.	Carbon Monoxide Cu. Mm.	No.
20	2.1	0.17×10^{15}	3.6	0.29×10^{15}
100	3.6	0.29	4.1	0.33
200	5.4	0.44	3.9	0.32
330	5.2	0.42	1.2	0.10

These values were found to be greater than those obtained by adsorption on mica and glass, but they never exceeded the amount required to form a monomolecular layer.

From Table II it is seen that in the case of oxygen the adsorption increases with rise of temperature, while with carbon monoxide the adsorption decreases. Experiments showed that the platinum saturated with carbon monoxide at 360° and allowed to cool adsorbed 6.9 cu. mm. of gas on its surface; 5.7 cu. mm. of this was removed by heating, but the remaining 1.2 cu. mm. was only removed by admitting oxygen. From these experiments, N_0 in this case was calculated to be 0.56×10^{15}, which corresponded fairly well with a monomolecular layer. In a somewhat similar manner it was shown that 5.9 cu. mm. of oxygen were adsorbed in the metal at 360°, which corresponded to $N_0 = 0.48 \times 10^{15}$. In further experiments the metal was saturated with the gas at 360° and allowed to cool, and the adsorption was the same. On heating to 360° no oxygen was driven off, so that the gas was apparently held on the surface of the metal much more firmly than the carbon monoxide. It could only be removed by reaction with the latter gas.

Langmuir considers that adsorption in the case of oxygen is due to strong forces of the nature of primary valence. In the case of carbon monoxide the bulk of the adsorbed gas could be removed by heating, but only with relative difficulty. This behavior was different from that of the adsorption of gases by mica and glass, which he considers to be due to valency forces of the secondary type.

To obtain some information about these two types of adsorption, some measurements of the adsorption of carbon monoxide and oxygen on platinum were made at liquid air temperatures. Carbon monoxide was introduced into the bulb until a pressure of 16 bars was reached, when the gas adsorbed was

4.8 cu. mm. The liquid air was then removed and the bulb allowed to heat up slowly. From pressure observations it was shown that 3 cu. mm. of gas adsorbed at liquid air temperatures was given off at a moderate temperature, and that the gas was readsorbed when the bulb approached room temperatures. From these experiments, Langmuir concluded that at liquid air temperatures the adsorption takes place by means of secondary (relatively weak) forces, and by moderately raising the temperature the gas comes off, but at room temperatures the reaction velocity becomes sufficient for the platinum to react (primary valence) with the carbon monoxide to form a much more stable adsorbed film. Similar experiments with oxygen showed that the adsorption increased steadily from about 0.6 cu. mm. at liquid air temperature to nearly 6.0 cu. mm. at 360°.

Much qualitative evidence for this theory of adsorption was obtained by Langmuir and is given in some of his earlier papers. Atomic hydrogen,[5] produced by heating a platinum wire in the gas at low pressures, was found to be strongly adsorbed on surfaces, giving films of remarkable stability, and from some experiments on glass surfaces he concluded (1) that adsorption is determined by chemical affinity; (2) the adsorbed layer does not exceed one atom in thickness; (3) hydrogen atoms striking glass surfaces are not reflected. Further evidence was obtained by some experiments with a tungsten filament.* Thus it was shown that at 3300° K. and a pressure of about 5 bars, 50 per cent of all the oxygen molecules which strike the filament react with it to form WO_3. At least one half of the surface must be covered with oxygen, and at this low pressure it is evident that the film has enormous stability and that probably the oxygen atoms are held to the tungsten by chemical forces.

The existence of this oxygen layer was confirmed by a study of the electron emission from the filament. A pressure of 0.001 bar of oxygen lowers the electron emission to a large extent. If a mixture of oxygen and hydrogen is heated in contact with a tungsten filament at 1500° K, the metal reacts with the oxygen as if no hydrogen were present. While this oxidation is going on, none of the oxygen and hydrogen react, and the WO_3 is not reduced by the hydrogen and no atomic hydrogen is produced. When the oxygen has been nearly all used up (partial pressure 0:01 bar), the hydrogen begins to disappear by being dissociated into atoms and effecting the reduction of the WO_3 (deposited on the bulb) (WO_3 distills from the filament at 1200° K.).

Langmuir considers that this experiment proves

(1) that in the presence of even 0:01 bar of oxygen the surface of the tungsten at 1500° K. is practically completely covered with oxygen.
(2) That this layer of oxygen will not react with hydrogen at this temperature.
(3) That such a layer of oxygen prevents the formation of atomic hydrogen.

It is quite obvious that this film has different properties from that of a film of oxide or a layer of compressed gas, and Langmuir considers that the oxygen atoms are chemically combined with the tungsten. The two primary valencies of the oxygen atoms are turned down to the metal, so that a hydrogen molecule striking the surface never comes in contact with the tungsten; but at the same time the hexavalent atoms of the latter are not completely saturated by the oxygen, so that they are still held firmly to the underlying atoms of metal. It is only when the surface layer of tungsten atoms becomes completely saturated by the oxygen that they cease to be held by these underlying atoms, and evaporate off as WO_3. In a film of this type the field of force lies completely below the surface, inaccessible to the hydrogen atoms; but when the pressure of the oxygen falls very low (0:01 bar), the rate of evaporation of the gas is greater than the rate of deposition, gaps are formed on the surface and the hydrogen is able to make a "flank attack" as it were, the oxygen film is suddenly removed and the dissociation of the hydrogen begins. Electron emission measurements show that the emission suddenly increases again at this point.

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* The pressure of gas in these experiments was under 5 bars.

Further observations confirmed these ideas. It was shown that in a mixture of carbon monoxide and oxygen the tungsten was oxidized as if none of the former gas were present. In fact, these gases refused to combine when the temperature of the filament was as high as 2800° K. Similar results were obtained with a mixture of methane and oxygen, which failed to react at 1800° K., the tungsten being oxidized. A tungsten filament decomposes methane, liberating hydrogen, and the carbon deposited being taken up by the filament, this decomposition also was found to be prevented by traces of oxygen. A tungsten filament decomposes ammonia at 1000° K., but if traces of oxygen are present, this does not occur at 1200° K. If a mixture of cyanogen and oxygen is heated to 1500° K., the oxidation of the tungsten is prevented until the cyanogen has been oxidized to carbon monoxide and nitrogen. Any excess of oxygen then reacts with the filament, or any excess of cyanogen reacts giving nitrogen and carbon, which is taken up by the tungsten. Thus it seems as if the cyanogen film is more strongly held even than the oxygen.

Experiments made on the electron emission from filaments confirmed the above views. In all cases with tungsten, chemically inert gases were found to have no effect on the electron emission, while nearly all gases which react with the metal were found to lower the emission. For instance, it was found that water vapor, which is almost as efficient a "poisoner" for the tungsten surface as oxygen, had as great an effect on the electron emission as the latter gas; while carbon dioxide, which reacts very slowly with tungsten and does not poison its surface, had hardly any effect on the emission.

Palladium, and to some extent platinum, occupy a unique position amongst metals owing to their ability to absorb relatively large amounts of hydrogen. Considerable work on the system PdH_2 has been recorded.

Holt, Edgar, and Firth[6] have put forward the view that the occlusion of hydrogen by palladium takes place in two distinct stages: firstly a very rapid occlusion (adsorption), followed by a slow occlusion (absorption). They conclude that the metal exists in two forms, the amorphous, which is responsible for the rapid initial adsorption, and the crystalline. The "activity" of the metal is largely conditioned by the presence of the amorphous phase. The latter is metastable, and the "activity" can be reproduced by heating the metal to a red heat in a vacuum, or by oxidizing the surface and reducing the oxide by hydrogen.

Andrew and Holt,[7] in a study of the heating and cooling curves of palladium in hydrogen, confirm these views; and they believe that the saturation value of the gas in the metal is the same, the difference being the rate at which the occlusion takes place. They found that in the absence of the amorphous film the rate is exceedingly slow, but at temperatures above 100° a rapid occlusion takes place in whatever form the metal may be, and at 150° all forms have an equal affinity for the gas.

Holt[8] has measured the rate of solution of hydrogen by palladium in the three different forms: (1) palladium black, (2) palladium foil 0:004 mm. thick, and (3) palladium foil 0.2 mm. thick. In cases (2) and (3) he finds that the curves consist of two distinct portions—a more horizontal branch which is considered to represent the rapid initial occlusion (adsorption), by the amorphous metal on the surface, and the second portion the diffusion of the gas into the crystalline metal. Andrew suggests that the adsorbed layer acts as a film of high concentration or high pressure of gas and effects the absorption of gas by the crystalline metal.

Although platinum black, like palladium black, has a high power for the occlusion of hydrogen, crystalline platinum appears to possess this property to a very small degree. An explanation for this fact has been suggested by Andrew[9] to be that in the case of palladium, the amorphous and crystalline phases can coexist in equilibrium up to a temperature of 250°, and that this is not the case with platinum.

Firth[10] has studied the occlusion of hydrogen by palladium at low temperatures and finds that adsorption only takes place. His conclusions may be briefly summarized:

(1) Below 0°—adsorption only.
(2) 0°-150°—adsorption followed by absorption.
(3) Above 150°—absorption only.

In a further communication[11] on the sorption * of hydrogen by amorphous palladium Firth has found that:

(1) The sorptive capacity of palladium black varies according to the method of preparation.

(2) Palladium black contains both amorphous and crystalline palladium, the proportion of each varying with the conditions under which it was prepared.

(3) The sorptive capacity of palladium black at low temperatures depends on the temperature at which sorption begins.

(4) Palladium black saturated with hydrogen at 100° sorbs further quantities of hydrogen when gradually cooled in the gas.

(5) A comparison of sorptive capacity at definite temperatures varying from 100° to — 190° shows a slight decrease from 100° to 20° and a continuous increase from 20° to — 190°.

(6) When palladium black is heated the proportion of the crystalline variety is increased.

Taylor and Burns[11a] have made some very interesting measurements of the adsorption of hydrogen, carbon monoxide, carbon dioxide, and ethylene in finely divided nickel, cobalt, iron, copper, palladium, and platinum, with special reference to the catalytic activity of these metals. They found that in the case of two samples of nickel the adsorption was considerable, and appeared to be independent of temperature from 25° to 218°. In the case of a third sample of nickel which had been reduced at a higher temperature the adsorption was greatly reduced. Their results for nickel are given below.

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* This term suggested by McBain is used to include both adsorption and absorption.

TABLE III

ADSORPTION OF GASES BY METALLIC CATALYSTS

Metal	Wt. in G.	Gas	Vols. of Gas per Vol. of Metal			
			25° C.	110° C.	184° C.	218° C.
Ni I	6.2000	N_2	—	—	—	—
		H_2	3.90	4.30	—	4.05
		CO_2	—	—	—	—
Ni II	13.9422	N_2	—	—	—	—
		H_2	4.15	3.90	—	4.00
		CO_2	1.15	0.50	—	0.40
		CO	—	—	3.50	—
		C_2H_4	4.10	3.50	—	2.55
Ni III	13.5210	N_2	—	—	—	—
		H_2	0.25	0.30	—	0.35
		CO_2	0.20	0.06	—	<0.05
		CO	—	—	0.75	—
		C_2H_4	0.65	0.35	—	0.15
Cu	22.8550	N_2	—	—	—	—
		H_2	<0.05	<0.05	—	<0.05
		CO_2	0.06	<0.05	—	<0.05
		CO	0.60	0.25	—	<0.05
		C_2H_4	0.65	0.25	—	<0.05
		O_2	<0.05	—	—	—
Co I	19.7600	He	—	—	—	—
		N_2	—	—	—	—
		H_2	<0.05	<0.05	—	—
		CO_2	2.00	0.50	—	<0.05
		CO	7.35	1.20	—	0.95
Co II	35.1750	N_2	—	—	—	—
		H_2	0.05	0.06	—	<0.05
		CO_2	0.50	0.05	—	0.05
		CO	1.55	0.60	—	0.35
		C_2H_4	0.35	0.10	—	<0.05
Co III	0.7500	N_2	—	—	—	—
		H_2	1.70	—	—	—
Fe	13.1030	N_2	—	—	—	—
		H_2	0.05	<0.05	—	<0.05
		CO_2	0.25	<0.05	—	<0.05
		CO	0.70	0.20	—	<0.10
		C_2H_4	0.30	<0.05	—	<0.05
Pd	0.6000	N_2	—	—	—	—
		H_2	753.25	540.50	—	—
		CO_2	<0.05	<0.05	—	—
		CO	14.40	14.40	—	—
		O_2	11.50	11.50	—	—
Pt. sponge	5.0000	N_2	—	—	—	—
		H_2	4.05	4.50	—	4.90
		CO_2	<0.05	<0.05	—	<0.05
		CO	0.20	0.85	—	0.45
		C_2H_4	<0.05	<0.05	—	<0.05
		O_2	1.90	2.80	—	4.30
Pt. Black	2.5000	N_2	—	—	—	—
		H_2	6.85	6.00	—	—
		CO_2	1.70	0.85	—	—
		CO	18.00	19.70	—	—
		C_2H_4	7.70	6.00	—	—
		O_2	26.50	26.10	—	—

Adsorptions by copper were of less magnitude than nickel and in no case were they measurable at 218°. Cobalt was found to adsorb small quantities of carbon monoxide, and adsorptions in the case of iron were very small. Platinum sponge and platinum black were found to behave very differently with regard to carbon monoxide and oxygen. Their results are shown in Table III.

They also found that the adsorbed film of carbon monoxide adhered most tenaciously to platinum, it being necessary to burn it off with oxygen and then remove the excess of oxygen with hydrogen.

Taylor and Burns conclude:

(1) That adsorption by such metals is a specific property quite different in nature from adsorption by inert adsorbents such as charcoal.

(2) The extent of adsorption is a function of the mode of preparation and is especially less pronounced the higher the temperature at which the reduced metal is prepared. The analogy of this fact with the corresponding facts of catalytic behavior is emphasized.

(3) Adsorption isotherms were studied in two cases: nickel and hydrogen, and copper and carbon monoxide. In both cases adsorption increases rapidly with increasing partial pressures below 300 mm. and becomes practically independent of pressure beyond this pressure.

They consider that the adsorption of gases by metals is a surface phenomenon "somewhat chemical in nature, possibly involving re-arrangement of electrons in both the adsorbent and the gas." They found that catalytic activity did not necessarily follow increasing adsorption, and in some cases they found an increase of catalytic activity at temperatures where adsorption had become almost negligible, from which they conclude the necessity of free evaporation of both reactants and resultants from the surface. They consider that adsorption alone is not the cause of many catalytic reactions, but that in addition the temperature factor must be considered.

Pease,[12] in connection with an investigation on the catalytic combination of ethylene and hydrogen in the presence of copper, has measured the adsorption of hydrogen, ethylene and ethane by a copper catalyst and found that the adsorption increased in the order hydrogen, ethane, ethylene. In his case he found a much greater adsorptive capacity than Taylor and Burns, viz., at 0° and 1 atmosphere, 3.0 c.c. of hydrogen and 8.0 c.c. of ethylene per 100 grams of metal.

In another communication Pease [13] has continued and extended his work on this problem. His results emphasize the marked specific nature of the adsorption, and he found that his data fitted approximately a modification of Langmuir's equation for adsorption in a single type of elementary space. His equation may be written:

$$V_{Ads.} = \frac{ap}{(1 + ap)} \cdot V_{sat.}$$

where a and $V_{sat.}$ are constants.

It follows from this, of course, that when ap is large compared with unity, then

$$V_{Ads.} = ap \, . V_{sat.} = p \times \text{a constant.}$$

and if ap is small compared with unity, then

$$V_{Ads.} = ap = p \times \text{a constant.}$$

Pease considered that elementary spaces of all degrees of activity were probably distributed over the surface of the catalyst, and that before Langmuir's formula can be applied the distribution curve for activity must be known. Assuming that these values can be grouped round three average values which correspond to (1) a high activity and a large value of a ($V_{Ads.} = V_{sat.}$); (2) a medium activity and a medium value of a; $\left(V_{Ads.} = \frac{ap.V_{sat.}}{(1+ap)}\right)$; and (3) a low activity and low value of a ($V_{Ads.} = apV_{sat.}$); we then have

$$V_{Ads.} = V_1 + V_2 + V_3 = V_{1sat.} + \frac{a_2p}{1+a_2p}V_{2sat.} + a_3V_{3sat.}p.$$

This equation was found to fit the values for hydrogen, carbon monoxide, and ethylene within the experimental error.

Pease also studied the poisoning effect of mercury, and the effect of de-activation of the catalyst by heat treatment. He found that mercury effected a decrease in adsorption in all cases, and that the decrease for hydrogen was twice as much as that for ethylene. He considers that the effect of the mercury is to saturate certain of the elementary spaces, and it appears as if the de-activation can occur in distinct steps, and that a center is prevented from adsorbing hydrogen while still adsorbing ethylene strongly.

Decreasing adsorptive power, in a general way similar, was observed in the de-activation by heating, but the decrease of the hydrogen adsorption was relatively less than in the case of poisoning, and the ethylene adsorption relatively more. In both cases (poisoning and heating), the strong adsorption at low pressures was considerably decreased while the additional adsorption at higher pressures suffered little.

Pease considers the adsorption to be specific between the copper and any particular gas, and that the activity of the surface is due to regions which contain atoms whose fields are highly unsaturated. He found that the heating necessary to cause the de-activation of the copper also caused a certain amount of sintering, which he considers to indicate the existence of atoms of high mobility and therefore unsaturation, and that one would be more likely to find such groups of atoms in "peaks" than in the valleys or capillaries.

Gauger and Taylor[14] have extended their work on the adsorption of gases by nickel, and have investigated the influence of temperature, pressure, and supporting material for the catalyst. The catalysts were made by the careful ignition of nickel nitrate with subsequent reduction in a stream of pure hydrogen. They were reduced at different temperatures and were supported in some cases on (1) diatomaceous earth, (2) diatomite brick. They found that the previous history of the metal had some influence on the adsorption, and that supporting it on an inert material increased the adsorption capacity tenfold, which they explain by the formation of increased surface; also that the catalyst in this form may be subjected to much stronger heating in the reduction process without decreasing its adsorptive capacity.

They determined the isotherms of hydrogen on nickel, and found the curves to be of the type of the normal adsorption isotherm with no discontinuities; but they found that at certain pressures a definite saturation capacity was reached at each temperature. They found also, as might be expected, that the saturation value diminished with rise of temperature, which means that the number of spaces which can be occupied by gas molecules is less at high temperatures. They consider that there are different adsorptive capacities of individual atoms on the metal surface.

HEATS OF ADSORPTION

Measurements of the heats of adsorption of gas have usually been determined with a view to comparing the values obtained at its boiling point.

Mond, Ramsay and Shields[15] determined the heat of adsorption of both hydrogen and oxygen on platinum black and obtained a value of 13880 cals/mol for the former and 35200 cals/mol for the latter. This value for oxygen agreed with the value found by Thomson for reaction

$$\mathrm{Pt} + \mathrm{O} + \mathrm{H_2O} = \mathrm{Pt(OH)_2} + 17900 \text{ cals.}$$

from which they concluded that the adsorption of the gas took place according to the above equation, the water vapor being always present in the platinum black.

More recent measurements have been made by Beebe and Taylor[16] who have determined the heat of adsorption of hydrogen on nickel and copper. They used two samples of nickel determined Q for each and again after heating for some time at 450° when the adsorptive capacity was found to be much reduced. The results are given in the table.

Sample	Determination	C.C. of H_2 Adsorbed	Q. Heat of Adsorption $\frac{\text{Cals.}}{\text{Mol.}}$
1. Before heat treatment..........	1	17.66	14.500
	2	16.21	14.210
	3	15.72	14.240
1. Heated 21 hrs. at 450°..........	4	7.86	20.300
	5	8.31	21.300
2. Before heat treatment..........	1	34.36	13.350
	2	35.35	13.700
2. Heated 4 hrs. at 450°..........	3	16.64	15.640
	4	15.81	15.350

From the above it is seen that Q is not even of the same order of magnitude of the latent heat of vaporization of hydrogen at its boiling point from which it is concluded that adsorption cannot be a simple condensation phenomena. It is also noteworthy that in both cases the heat of adsorption is considerably higher when the metal possesses a lower adsorptive capacity. Rideal[18] from other considerations has calculated the heat of adsorption of hydrogen on nickel to be 12000 calories per mole which agrees fairly well with Beebe and Taylor's experimental determined values.

Quite recently Palmer[17] by a very ingenious method has used the coherer to investigate adsorption films. Using contacts between fine filaments of (1) tungsten, (2) platinum, (3) carbon and platinum, he determined the critical voltage to remove the film and establish metallic contact, and from this the energy of desorption of the film can be calculated. Although certain assumptions have to be made in this calculation, it is claimed that such a method has the advantage over calorimetric determinations inasmuch as it is possible to produce a clean filament surface and to test its cleanness and also as gases dissolved in the metal are unlikely to play any part in increasing the electrical resistance of the contact the heat of adsorption can be distinguished from heat of solution. Palmer's results are given in the table.

Heat of Desorption per Gm. Mol. (Cal.)

	Tungsten	Platinum	Carbon
Oxygen	10,800	1,200	—
Hydrogen	166	160	—
Carbon monoxide	32,000 (maximum)	750	—
Nitrous oxide	Very small	—	—
Nitric oxide	950	950	—
Ammonia	7,300 (maximum)	—	—
Sulphur dioxide	8,100 (maximum)	5,340	—
Carbon dioxide	Very small	—	Very small.
Water vapor	40,000 (maximum)	—	—
Ethane	Very small	—	5,400
Ethylene	Very small	—	2,550
Acetylene	Very small	—	4,900

These values are in most cases very close to the latent heat of evaporation of the liquefied gas at its boiling point but Palmer very rightly points out the difficulties of comparing adsorption in such cases with simple condensation when it occurs at temperatures so far above the boiling point of the gas and in some cases above the critical temperature. In addition, nitrogen, carbon dioxide and nitrous oxide are desorbed from tungsten with almost zero latent heat.

It may be mentioned that a theory of adsorption first put forward by Eucken[19] and afterwards developed by Polanyi involves very different assumptions from those of Langmuir. The most important of these is that the adsorbed surface does not consist of a single layer of atoms or molecules but consists of an envelope whose density varies continuously from the surface outwards and at every point a function can be defined which expresses the adsorption potential, *i.e.*, the work done in transferring unit mass of the adsorbed substance from that point to infinity.*

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* See also references to Gouy's theory in index. J. A.

Fluidity and Plasticity

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Perhaps no one any longer regards viscosity as being an additive property in true solutions, yet, due presumably to force of habit, data on flow are still expressed in terms of viscosities instead of the more useful fluidities. The difference is particularly striking in the study of colloids, and may be illustrated by a wide variety of suspensions or emulsions. We will take as our example the dispersions of Trinidad asphalt in benzene studied by C. Richardson.[1] The first additions of asphalt to benzene are of very slight effect upon the viscosity, but as the concentration increases the effect is greater and greater until finally the viscosity becomes infinite. This behavior is quite general and remained unexplained until the fluidities were plotted against the concentration, when it was observed that in this and many other cases the fluidity-concentration curve is linear. The mystery as to why the viscosity increases so much more rapidly in the more concentrated solutions is therefore explained by the mathematical requirements of the case which may be summed up in the following law. Whether the solution be a true solution or merely a colloidal dispersion *each successive equal increase in the concentration of the solute decreases the fluidity by a constant amount until the fluidity reaches that of the pure solute, i.e.,* zero in the case of most colloids. The discovery of this simple law opens up the road to further discoveries, for departures from the linear curve can be readily determined. As a matter of fact there are very important cases in which the simple law does not hold, as when the solute and the solvent unite together to form a chemical combination; and in this case we have the possibility of estimating the amount of chemical combination by means of a fluidity method. To compare a family of hyperbolas using only viscosities may be entirely practicable from a purely mathematical standpoint, but as the curves become no longer simple hyperbolas the problem becomes vastly complicated and it is far simpler to use fluidities and the graphical method.

In Fig. 1 the curve *AC* represents the viscosities observed by Richardson and the curve *ac* represents the corresponding fluidity curve. Purely for diagrammatic purposes the curve *bd* representing the same solution at a lower temperature has been added which bears a very obvious relation to the curve *ac*. By plottting the reciprocals of these assumed fluidities we arrive at the curve *BD* which bears no *obvious* relation to Richardson's curve *AC*. This illustration is given to emphasize the importance of comparing additive properties wherever practicable.

When one studies the fluidity-concentration curves of colloidal solutions, as illustrated in Fig. 1, one becomes struck with the fact that the fluidity, as ordinarily measured, reaches a zero value at a definite concentration which *seems* sharply to demarcate viscous from plastic flow. The italicization of the word "seems" is justified by the discovery that the viscosity of colloids, as ordinarily measured, is merely *apparent* viscosity, and not viscosity at all in the sense of being a fundamental physical constant independent of the instrument in which the viscosity was measured. Abundant experiments have now proved that many and perhaps all colloids have the disagreeable quality of exhibiting viscosities, as measured in the customary manner, which vary with the shearing stress. Thus Glaser found that a solution of colophonium in turpentine showed a viscosity which varied from 4.2×10^7 poises to many times that value without any change in concentration or temperature, dependent merely upon the shearing stress employed. Since colloids do not appear to have a definite melting point, boiling point or solubility—properties which are most useful for control in classical chemistry—it is a pity if perhaps the most outstanding property of colloids, viz., the viscosity, proves to be a false guide; and certainly it would be unsafe to make broad generalizations based on a property which is dependent upon the dimensions of the instrument used in measuring the property, but according to some unknown law. If it could be shown that the *apparent* viscosity is not a fundamental property of colloids at all, but a mixture of two or more properties, then the lack of control properties in colloid chemistry would be more than made good, and our knowledge of colloid chemistry might be expected to expand correspondingly.

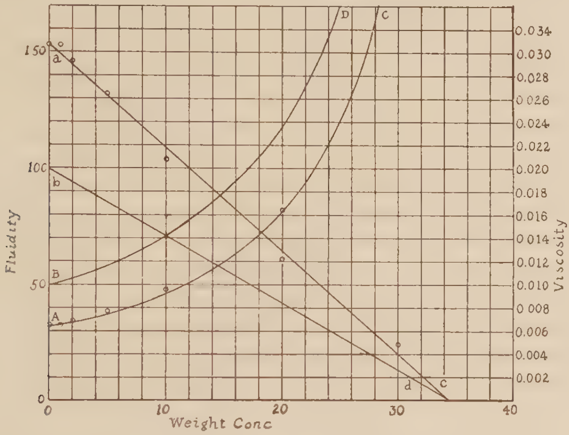

FIG. 1.—Apparent viscosity curves of asphalt dissolved in benzene at two different temperatures *AC* and *BD*. The same data plotted as fluidities *ac* and *bd* discloses obvious relationships.

When a viscous substance, either a liquid or a gas, is subjected to shearing stress, a continuous deformation results which is, within certain restrictions, directly proportional to the shearing stress. This fundamental law of viscous flow is represented diagrammatically by the curve *OA* in Fig. 2. It can be demonstrated that the slope of the curve *OA* is a measure of the fluidity. There is some flow at every shearing stress, but at the smallest shearing stresses the time required for a given amount of flow is very great, hence pitch, which would require very great stresses to shear it rapidly, nevertheless moves continuously so that it loses its shape and takes the shape of the containing vessel.

Solids on the other hand maintain their shape through long periods of time, and this is particularly conspicuous in very soft solids like clay which can be very readily and quickly deformed by forces only a little greater than those which the material is able to resist completely. This behavior can be represented diagrammatically by the curve *BC* in Fig. 2. The distance *OC* represents the shearing stress required to overcome the *"yield value"* and the slope of the curve *BC* is a measure of the mobility of the plastic material.

So far as is known at present these properties are probably independent of the dimensions of the instrument in which they are measured, but there are some discrepancies and much more work is needed on this phase of the subject. The yield value and the mobility are properties which appear to be entirely independent of each other, so that it is not likely that any attempt to combine them in such a way that the plasticity can be represented by a single numerical quantity, will meet with success. Plasticity, hardness, malleability, ductility are therefore properties which, when applied to soft solids, are complex and cannot be properly represented by a single numerical quantity; but they can be defined and measured with precision in terms of yield value and mobility. Thus there are different kinds of hardness. A solid having a low yield value and a low mobility possesses an entirely different kind of hardness from one which possesses a high yield value combined with a high mobility. The former would appear to be the harder under a heavy blow of very short duration while the latter would show the greater hardness under a light load applied for a long time.

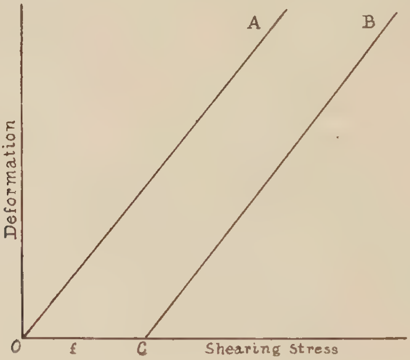

FIG. 2.—Viscous and plastic flow.

It is most unfortunate that the viscosities of colloids recorded in the literature were for the most part made at one shearing stress only, so that the yield value and mobility cannot be calculated without further experimental work. But if further work will give us an insight into the properties of all sorts of solids which was completely denied as long as "apparent viscosities" alone were considered, we need waste no time in vain regrets, but rather rejoice in the hope that new experiments will prove more fruitful.

Reverting to Fig. 2, we know that the curve *OA* is linear only under certain limitations and when certain important corrections are made for kinetic energy losses, end effect, slippage, etc. The curve applies only to linear as distinguished from turbulent flow. In the case of the curve *BC*, for plastic solids there are also certain corrections and limitations; but our knowledge of plastic flow is so recent that the nature of these corrections and limitations has as yet been very imperfectly formulated. In some of our experiments the curve has appeared to be quite linear whereas in others it has appeared to be linear only at the highest shearing stresses. At very small shearing stresses—far below the yield value as found by extrapolation—there is often some small deformation. When we have a heterogeneous material consisting of fine solid particles suspended in a very fluid medium, we should expect the medium to filter through the mass as a whole, hence a correction for *seepage* is called for. Even in the case of the hard metals we know that Hooke's Law is not fully obeyed so that continuous deformation takes place very slowly, at loads far below the yield value. Up to the present the best way to avoid making a seepage correction has appeared to be by using stresses so great that the curve BC is linear over a sufficiently extended range so that extrapolation can be made with safety. As our knowledge is amplified it is hoped that the necessary corrections may be made directly. In this general survey no attempt will be made to acquaint the reader with the different forms of apparatus for the measurement and calculation of the yield value and mobility, but assuming that we have available these two fundamental properties, how can they be utilized to advantage?

It has already been shown how hardness may be regarded in an entirely new light when it becomes customary to express it in terms of yield value and mobility. The plasticity of clay, lime, plaster, road building materials is obviously important and should be capable of measurement, and probably it can be measured in each of these cases in terms of yield value and mobility.

Lord Kelvin held the view that elasticity of shape is exclusively a property of solids. When a body is subjected to shearing stress, it is *immediately* deformed and an opposing stress developed, so that energy is stored up within the body. The greater this deformation the greater the *elasticity* and the smaller the reciprocal *rigidity*. If on removing the shearing stress all of the energy used in producing the elastic deformation is recovered, the body is said to be perfectly elastic. If some time elapses before the shearing stress is removed, viscous or plastic flow takes place and the strain originally existing as elastic deformation becomes permanent with a dissipation of the corresponding energy as heat. What Lord Kelvin called imperfection of elasticity we should now call simply plastic flow. His view that liquids cannot have elasticity of shape is confusing and unnecessary. Glass, for example, is generally regarded as an undercooled liquid and yet it is generally regarded as highly elastic. As a matter of fact we are forced to regard elasticity as a property which is entirely independent of fluidity or plasticity. Nevertheless elastic and plastic or viscous deformations are often associated together so that they should be distinguished the one from the other. This is fortunately very easy, for elastic deformations are independent of the time factor upon which the others depend. To measure the elastic deformation in either solids or fluids it is necessary to choose a time before the energy stored up as elastic deformation has had time to dissipate itself appreciably either as viscous or plastic flow.

While in the above example, a knowledge of the character of plastic flow was necessary in order to distinguish the elasticity which is entirely independent from plasticity, we may now consider briefly a few properties which are closely dependent upon plasticity.

The property of melting point when applied to colloids seems not to be very highly regarded, on the assumption that colloids do not have a definite melting point capable of determination; yet in spite of this a large number of melting point methods have been devised which are in constant use, and it is known that a given method will often give values agreeing to a few tenths of a degree.

Two different principles [2] have been made use of in the determination of the melting point. According to the one, the cooling curve is obtained and the melting point located by the breaks in the curve. According to the second, observations are made of the temperature at which the material flows in a specified manner. Reference may be made to a few out of the great variety of methods which have been suggested.

(a) In the classical method, flow is produced by surface tension assisted by gravity; but when the melted substance has a very high viscosity or possibly a yield value, it is difficult to determine when the melting begins. For butter, Wiley used discs floating between layers of alcohol and water.

(b) Usually gravity alone is depended upon to exert a shearing stress. In the method of Pohl, the material adheres to the bulb of a thermometer and as the substance is heated the melting point is taken as the temperature at which the first drop falls from the thermometer. In the method of Herold, the material is placed in a thin glass tube and allowed to solidify around a thermometer. As the system is warmed, the melting point is taken as the temperature at which the material separates from the thermometer. In the ball and ring test the weight of the ball exerts a shearing stress upon the material supported in the ring.

(c) The Saybolt method depends upon the buoyant force of water acting upon wooden pins which are held in place in holes in a brass plate by means of the solid whose melting point is required.

(d) Thus far no one seems to have used plasticity measurements for the determination of the melting point.

Theoretically we should expect a mixture of two simple substances A and B to begin to melt as soon as the eutectic point or temperature of incipient fusion is reached. On further heating, the hard material will become soft but it will remain plastic if one of the components (B) is present in excess of the eutectic mixture, there being present a suspension of B in a saturated solution of B in A.* As the temperature is raised the solid phase will gradually disappear, and at the temperature of complete fusion the yield value which has been gradually decreasing will entirely disappear, and the plastic solid will become a viscous liquid. There are therefore two transition temperatures and these are very sharply marked in the plasticity curves plotted over this range of temperature.

As the temperature of a solution is lowered we should expect to find the same temperatures in reverse order but now called the *temperature of incipient solidification* and of *complete solidification*, and numerous methods have been proposed for getting the *setting point* without usually stating whether one of the above temperatures or some other is being determined. As a matter of fact the methods in use for both melting point and setting point, use widely different shearing stresses; hence we should not expect them to locate the temperature of complete solidification where the yield value is very great, or the temperature of complete fusion where the yield value is very small; and since there is a wide difference in the shearing stresses employed in the various methods, we should not expect the different methods to agree with each other. This expectation is so fully realized that Lewkowitsch [3] says, "A table in which the various melting points (of fats) were set out would show so glaring a disagreement between various observers, that for practical purposes I consider it useless to collate the numbers here."

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* This seems to justify the view that in metals we frequently meet the colloidal state; for in quickly chilled metals the suspension of B may contain many particles of colloidal dimensions. Even where larger particles have been formed, colloidal dispersion must again be met in the reverse process of fusion. J. A.

Perhaps the most serious difficulty in obtaining the two transition temperatures referred to above, is due to the undercooling and superheating which are so frequent in colloidal solutions. Superheating does not trouble at all when dealing with pure substances, and undercooling is not particularly troublesome when the fluidity of the melt is high. But unfortunately both difficulties have to be faced when dealing with colloidal solutions. The plasticity of a well-stirred solution has been observed to change for hours, and it may be assumed that the plasticity of a substance like glass will continue to change for years. The plasticity method has the advantage over the other methods which have been suggested in that the temperature may be kept uniform, if desired, until equilibrium is reached. By measuring the yield value and mobility over a range of temperatures it is practicable to find the points of discontinuity in the curves.

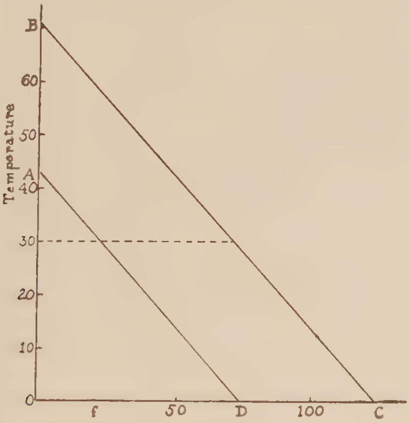

FIG. 3.—Temperature-yield value curves of the same solute in different solvents. The yield values at a given temperature may be a measure of colloidal "solubility."

We may refer very briefly to one further property which is ordinarily supposed not to depend upon plasticity, viz., *solubility*. It is customary to speak of the solubility of emulsion colloids in certain "solvents." Thus it is commonly stated that nitrocellulose is more soluble in acetone than in, let us say, butyl acetate; but the nitrocellulose does not form a true solution; and if there is no limit to the amount of the nitrocellulose which either medium will peptize, then the question arises, "What is meant by saying that acetone is the better solvent?" To be sure, the "better solvent" gives a solution having a higher apparent fluidity; but since the *solvents* differ widely in fluidity, this again is not very surprising and it is not very enlightening either.

If one measures the yield value and mobility of dispersions of the same nitrocellulose in both media over a range of temperatures, it is found that the yield value decreases as the temperature is raised so that at a certain temperature characteristic of each solvent, the yield value becomes zero. This temperature therefore corresponds to the passage from a plastic solid to a viscous liquid. It therefore corresponds to the temperature of complete fusion discussed above. The data obtained show that the mobilities in different media are proportional to the fluidities of the media, but the yield values at a given temperature are quite different and it is believed that the magnitude of the yield value is a measure of the amount of the colloid in the gel condition. The "solubility" is therefore the greater as the yield value is smaller. If the curve *BC*, Fig. 3, represents the temperature-yield value curve for a nitrocellulose dispersed in ether-alcohol mixture and the curve *AD* the similar curve in acetone, we would infer that acetone is the better peptizing agent at all temperatures. Were the curves *BC* and *AD* not parallel, as is actually the case, but converging, it would indicate that at some temperature the ether-alcohol mixture would be the better "solvent."

The cases described will perhaps serve to illustrate the possible uses of the plasticity method in working out the theory of colloids as well as in furnishing control properties in their industrial application.

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The indefiniteness of "melting point" is referred to by G. Friedel. See his paper in this volume. J. A.

Consistency *

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1. Introduction

It is generally considered that there are three states of matter, gaseous, liquid and solid, but it is often difficult to distinguish between liquids and soft solids. The distinction between a liquid and a soft solid is often drawn on a basis of what is termed consistency. It is not necessary to speak of the consistency of gases since all gases may be readily recognized as such. Nor is the term consistency necessary for materials hard enough to be tested by the methods employed in determining the hardness of metals.

How many factors determine consistency is still a matter of controversy, but the colloquial meaning of the word is well understood and may be illustrated by the description, from a recent novel, of Flanders mud after a thaw. "As the flow of water increased, the sides of the trenches began to fall in; the earth thus mixed with the water thickened it to a consistency which might be likened to very rich soup." Expressed in more scientific language, by the addition of earth to water its consistency is changed from viscous to plastic.

2. The Distinction Between Viscous and Plastic Materials

Viscosity is defined by the force which will move a unit area of plane surface with unit speed relative to another parallel plane surface from which it is separated by a layer of the liquid of unit thickness. An equivalent definition of viscosity is the constant ratio of shearing stress to rate of shear. In first suggesting the term poise for the cgs unit of absolute viscosity, it was pointed out by Deeley and Parr[1] that in the case of a soft solid or plastic substance the "so-called viscosity" is not the same for all rates of shear, whereas the viscosity of a liquid is a constant and should be named. In the present paper this "so-called viscosity" will be referred to as the apparent viscosity. A material will be considered plastic if the apparent viscosity (the ratio of shearing stress to the rate of shear) varies with the rate of shear, and will be considered viscous only when this ratio is found to be constant.

The cgs. unit of absolute viscosity is known as the poise, the centipoise being one hundredth of a poise. The reciprocal of the absolute viscosity is known as the fluidity. Under certain circumstances the ratio of the absolute viscosity to the density in grams per cubic centimeter is an important quantity and is called the kinematic viscosity.

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It has been found for true liquids that within the limits of experiment and at ordinary rates of shear, the ratio of shearing stress to rate of shear for a given temperature and pressure is constant. Even at abnormally low rates of shear there is little or no evidence of a variation in this ratio in tests of homogeneous materials.[2] Hence in tests of such materials, a variation in apparent viscosity must be taken as indicating experimental error.[3] In tests of other materials, a variation in the apparent viscosity [4] should be taken as an indication that the materials are plastic. Since with a viscous material the ratio of shearing stress to rate of shear is a constant, viscosity can be expressed by a single numerical value, but the consistency of a plastic material must be expressed by an equation or other means which completely defines the variable relation between rate of flow and the force which produces it.

It is to be expected that true solutions and mixtures of miscible liquids will be viscous, but that mixtures of a liquid with a powder or finely divided material will be plastic, if of sufficiently high concentration. In cases of doubt tests are necessary, the essential requirement being that successive trials should be made at different rates of shear. The standardization of the rate of shear, as has been proposed,[5] may enable different laboratories to obtain the same numerical results, but the complete relation between the rate of flow and the force which produces it cannot be obtained by a single test. Two different plastic materials which show the same apparent viscosity on a single test would not necessarily have the same consistency.

If one plastic material had a high "yield value" and high "mobility" and another had lower yield value and lower mobility, they might show the same apparent viscosity on a single test, but would not have the same consistency. The terms yield value and mobility will be explained later in the section on measurement of plasticity, but it is necessary first to consider the simpler case of the measurement of viscosity.

3. The Measurement of True Viscosity

In torsional instruments of the constant deflection type, like the MacMichael,[6] the liquid is placed in a cup which rotates at constant speed, causing the deflection of a torsional pendulum whose bob is immersed in the liquid. In other rotary instruments the outer cylinder is still and an inner cylinder is revolved by means of a weight, or weights. The Stormer is the best known instrument of this type.

Comparatively few experimenters who have used a torsional or other rotary viscometer have apparently been aware of the distinction between viscosity and plasticity, and it is the failure to make this distinction to which must be largely attributed the confusion in regard to consistency with which the colloid chemists are now struggling.[7] Exceptions to this rule are Hatschek, whose work will be considered later, and Perrott and Thiessen [8] who observed, by varying the speed of a MacMichael viscometer, a variation in the apparent viscosity of a mixture of linseed oil and lampblack with a variation in speed.

In the efflux method the time is measured for a given volume to discharge through a short tube or capillary. As this method has been most thoroughly investigated for the measurement of consistency, both viscous and plastic, attention will be confined to the methods of calculation employed with this method. The fundamental equation for the flow through a capillary tube, as first determined experimentally by Poiseuille and amplified by Couette[9] and others, is

$$\mu = \frac{\pi g d^4 P t}{128 Q (l + \lambda)} - \frac{m \rho Q}{8 \pi t (l + \lambda)}. \qquad (1)$$

where μ = viscosity in poises
d and l = diameter and length of capillary in centimeters
$\frac{Q}{t}$ = rate of flow in c.c. per second
g = acceleration of gravity = 981 cm. per sec.^{2}
P = average difference in pressure, in grams per cm.^{2}, between the two ends of the capillary = ρh when produced by a head h in centimeters of liquid of density ρ in grams per c.c.
m = coefficient of kinetic energy correction
λ = difference between the measured and effective length of capillary = Couette correction.

The coefficient m may be taken as 1.12 for long capillaries with submerged discharge and as 1.00 for technical short tube viscometers with free discharge. The corresponding values for the Couette correction are 0.8 d and 0.5 d. Errors due to inaccuracies in the selected values of m and λ may be made negligible by using long capillaries and low velocities of flow.

A common error is to neglect the kinetic energy correction entirely and to assume that the viscosity is proportional to the time of flow. A more serious error is to use too short a capillary so that the flow is turbulent. It is usually assumed that there will be no turbulence if

$$\frac{v d \rho}{\mu} < 2000 \qquad (2)$$

where v is the average velocity of flow in centimeters per second. The constant, 2000, is approximately correct for long tubes, but has a lower value for short tubes. For tubes of seven diameters in length, as in the Engler and Saybolt Universal viscometers,[10] it is about 800, and according to Sheely[11] the value is approximately 1200 for a capillary 30.5 diameters in length. The exact law of variation of critical velocity with dimensions of capillary is not known.

Now if μ is calculated from Equation (1) for tests at more than one rate of flow, and a constant value is obtained, then μ is the viscosity of the liquid at the temperature of test. If however μ is found to vary with the rate of flow, but a constant value is obtained at any one rate, the material must be plastic. It then requires more than one numerical value to express the consistency (plasticity) of the material.

4. The Measurement of Plasticity

With viscous materials the slightest pressure, P, will produce flow, although the rate of flow may be very slow with low pressures applied to very viscous materials. With plastic substances (according to the simplest theory which seldom if ever applies without complications) the flow is proportional to the pressure in excess of a certain minimum pressure p called the yield value, which is required to start the flow. Bingham[12] first gave the following approximate equation for flow of a plastic material through a small tube.

$$\frac{1}{M}=\frac{\pi g d^4 t(P-p)}{128Ql} \tag{3}$$

where M is the mobility and the kinetic energy correction has been omitted because ordinarily negligible. The Couette correction has been omitted because its value cannot be estimated, although, as will be seen later, it is not always negligible. It will be noted that if the above mentioned corrections are neglected in Equation (1) and $p=$ zero in Equation (3), then $\frac{1}{M}=\mu$.

If tests are made of a plastic material with a capillary tube viscometer in which the pressure can be varied, then if the pressures are all high enough, there will be a linear relation between rate of flow and pressure, which appears to be in agreement with Equation (3). The graph would differ from similar results with a viscous liquid in intersecting the pressure axis at a distance p from the origin. Hence the apparent viscosity, represented by the slope of a line connecting any point on the graph with the origin, would be a variable.

It will be seen that according to Equation (3) there are two physical constants which determine the consistency of a plastic material. It is interesting to note from the work of Bingham and Jacques,[13] also with paint, that the yield value and mobility appear as distinct properties, so that a given ingredient may affect one but not the other.

Bingham observed in testing clay slips as well as paints that there was a tendency for the straight graph, indicated by Equation (3), to bend toward the origin at the lower end. He attributed this to seepage, and believed that the best way to overcome the difficulty was to use high pressures and capillaries of small diameter so that the test points would lie in the straight portion of the graph. It was found however by Green,[14] by microscopic observations on the flow of paint in capillary tubes, that at low pressures the material in the capillary moved as one solid plug, and that at higher pressures the paint moved "in telescopic layers, the inner ones at a much higher velocity than the outer ones."

Green's observations lead Buckingham[15] to correct and modify Equation (3), thus obtaining the equation

$$\frac{Q}{t}=\frac{\pi g d^4 M}{128l}\left(P-\frac{4}{3}p+\frac{p^4}{3P^3}\right)+\frac{\pi d^3 \varepsilon \varphi P}{16l}. \tag{4}$$

The last term takes account of viscous slip at the boundaries, it being assumed that there is a very thin lubricating layer of liquid of the thickness ε and fluidity φ between the plastic material and the wall, and that this layer adheres to both the wall and the plastic material.

Equation (4) indicates that below the pressure p the flow, due entirely to slip, increases directly as the pressure. At the pressure p shearing begins, and the relation between flow and pressure would be shown by a curved graph which approximates a straight line at high pressures. Interesting experimental confirmation of the existence of these two régimes of flow is furnished by de Waele[16] who first accepted and afterwards repudiated Equation (3) and who ignores Equation (4).

According to Bingham[17] it is preferable when $\frac{Q}{t}$ is plotted against P to report the intercept on the pressure axis as a yield shear value f which may be calculated from the yield value p by the equation

$$\frac{f}{p}=\frac{F}{P}=\frac{d}{4l} \tag{5}$$

where F is the shearing stress at the walls of the capillary, in grams per square centimeter, due to any pressure P, and f is the corresponding value when $P=p$.

Considerable space has been given to the method of expressing consistency by yield shear value and mobility because this has been the method most widely used in this country.[18] However, difficulty has been experienced in obtaining check results with capillaries of different dimensions, especially with emulsoids.[18a] Exponential equations for the relation of flow to pressure were early proposed by Nutting, de Waele and others, but it is only within the last year that exponential equations have been used to any great extent.[18c] It is as yet impossible to predict which form of equation will survive. In the light of present knowledge, it seems quite possible that any one method or equation for expressing the consistency of a plastic material may not have universal application. Indeed, each separate class of materials may demand individual treatment.

It has been found experimentally that the rate of flow in cubic centimeters per second is given by

$$q=kP^n \tag{6}$$

where n is a constant of the material, which is greater than unity unless the material is viscous, and k is an unknown function of another constant of the material and of the dimensions of the capillary.

Farrow and Lowe [18d] conclude, from tests on starch pastes, that

$$k=\frac{\pi g^n d^4}{128e(\mu)} \tag{7}$$

where (μ) is the second constant of the material, which, like n increases with the concentration. This value of k, like equation (6), is purely empirical, and no assumption has been formulated from which it could be mathematically derived.[18e]

It was pointed out by Green [18f] that with stiff paint pastes and small capillaries, flow may not begin until a definite starting pressure has been reached. Porst and Moskowitz [18g] found this to be true also for certain starch pastes. With such a paste, the logarithmic flow-pressure graph is convex upward. To make equation (6) more general, therefore, it must be modified to

$$q=k\,(P-A)^n \tag{8}$$

where A is the starting pressure which may be found by direct observation or chosen by trial and error as that value which will give a straight graph when the logarithm of q is plotted against the logarithm of $(P-A)$. Finally, by combining equations (7) and (8),

$$(\mu)=\frac{\pi g^n d^4(P-A)^n}{128eq}$$

where (μ) and n are two empirical constants which may be used to define the consistency of a plastic material.

5. DIFFICULTIES IN MEASURING THE CONSISTENCY OF PLASTIC MATERIALS AND SOFT SOLIDS

As has been mentioned, seepage may be a cause of difficulty in measuring plasticity by the capillary tube method. According to Hall [19] a similar trouble is experienced with the MacMichael viscometer as tests of clay slips were not reproducible, due to what might be called a "puddling effect." The material immediately surrounding the pendulum bob changes in consistency as the stirring continues.

There appears to be no reason for assuming that the slipping which takes place at low pressures in a capillary tube does not continue after the telescopic flow has commenced, so that there is flow of both kinds simultaneously at high pressures, according to Equation (4). On the other hand Equation (3) could only be justified on the supposition that there was no slipping at high pressures.

The most serious difficulty with the capillary tube method when applied to very stiff or hard plastic materials is that due to end effects. In deriving Equations (1) and (4) it is assumed that all resistances to flow, outside the capillary, are negligible, and in many cases this is entirely justifiable. There is little difficulty in using a capillary long enough to render λ negligible in Equation (1). Equation (4) gives satisfactory results when applied to tests with clay slips and paints which appear to be liquid but are in reality plastic, as may be proved by test, but this equation fails completely for stiff clays and fats, even when the consistency is not changed in passing through the capillary.

In a passage often quoted to distinguish a plastic from a viscous substance, Maxwell[20] implies that all plastic materials are elastic at stresses below a certain value, for he says, "if the form of the body is found to be permanently altered when the stress exceeds a certain value, the body is said to be soft or plastic, and the state of the body when the alteration is just going to take place is called the limit of perfect elasticity."

The elasticity of materials possessing both elastic and viscous properties has been investigated by a few experimenters, but there is no general agreement as to the best method to employ. The subject has been investigated mathematically by Butcher,[21] but unfortunately he made no tests and gives only the one example that when the stress exceeds the elastic limits of some of the molecules, metals are elastico-plastico-viscous, and they partially recover from deformation if stressed for a short time.

Barus[22] by tests with a capillary tube and Michelson[23] by tests on cylindrical rods in torsion, have observed elastic effects in soft or plastic solids. Perhaps the most striking tests are those of Schwedoff[24] with a torsion viscometer. He found that if the stress was slight enough and not too long prolonged, a solution containing only 5 grams of gelatine to 1 liter of water was perfectly elastic, but glycerine and sugar solutions showed only the phenomena of viscous liquids. Glycerine and sucrose solutions are recognized standards of viscosity, but as will be seen later, gelatine is a colloidal material which is typical of the class which, in high enough concentrations, form an elastic jelly. According to Schwedoff "the higher the elastic limit, the more perceptible is the variation in viscosity. Viscosity is not constant except for the liquids which show no trace of elasticity in shear." It should be remembered that Schwedoff speaks of apparent viscosity simply as viscosity.

6. BINARY SYSTEMS

When a material is very finely divided and is in permanent suspension in a solid, liquid or gas (the dispersion medium), the heterogeneous mixture is called a dispersoid. Omitting the case of a mixture of gases as not a true dispersoid, there are the 8 possible types of dispersoid shown in Table I.

TABLE I

TYPES OF DISPERSOIDS

Type No.	Disperse Phase	Dispersion Medium	Example
1	Solid	Solid	Ruby glass
2	Liquid	"	Water of crystallization
3	Gas	"	Meerschaum
4	Solid	Liquid	Metals in colloidal state
5	Liquid	"	Emulsions
6	Gas	"	Foam
7	Solid	Gas	Smoke
8	Liquid	"	Clouds

A colloidal solution may be somewhat arbitrarily defined as a dispersoid in which the diameters of the particles lie between 0.0001 and 0.000001 millimeter (usually written 0.1 μ and 1.0 μμ). Mixtures with larger particles would be called coarse suspensions and smaller particles would be found in molecular solutions. Colloids, as for example albumen or gum arabic, have a slow rate of diffusion, while crystalloids, such as sodium chloride or hydrochloric acid, diffuse more rapidly into pure water. The former may be separated from the latter by the process known as dialysis, by means of a membrane or "ultra filter" through which crystalloids pass easily but colloids will not pass.

It must constantly be remembered in reading works on colloidal chemistry that the distinction between viscous and plastic materials has not generally been recognized, although as pointed out by Hardy,[25] the matter has been occasionally discussed since 1851.

> "I ventured to point out in 1899 (*The Jour. of Physiology,* 24, 180) that the high viscosity of colloidal solutions is probably of complex origin and that its magnitude is very imperfectly analyzed by ordinary methods of measurement. If colloidal solutions are heterogeneous states of matter, the viscosity as measured by the flow in capillary tubes will be in part due to the influence of the friction of internal surfaces on the fluidity—a point which as I then drew attention to, was discussed as early as 1851 by Frankenheim (*Jour. f. prak. Chem.,* 54, 433). Transpiration methods measure fluidity, and this will only be simply related to the true molecular internal friction in homogeneous fluids."

Hardy does not have in mind the variable pressure methods described in the section on plasticity, since in the "ordinary methods of measurement" with capillary tubes, observations are made at only one pressure. It was impossible by such methods to determine whether a material was viscous or plastic, and it is only in rare cases when an experimenter recorded whether or not the apparent viscosity varied with the rate of shear, that it is possible to ascertain whether the material which he was testing was plastic or viscous.

According to Clayton,[26] who makes no distinction between viscosity and apparent viscosity,

> "The position regarding the viscosity of emulsions from a quantitative point of view is far from satisfactory, very little work having been done in this connection. Dilute two phase emulsions show a viscosity not much greater than that of water. Viscosity increases rapidly as the volume of the dispersed phase increases, but in this case of course, there arises the new factor of the presence of the emulsifying agent."

Bingham[27] regards it as probable that viscosities in emulsions are additive, but it is difficult to reconcile this rule with the fact that the apparent viscosity of an emulsion has been found to depend upon the size of the particles. Buglia,[28] for example, found that the apparent viscosity of milk is increased by the process of homogenization, which decreases the size of the fat globules, but the apparent viscosity of skimmed milk was unchanged by the process. According to Alexander [29] there appears to be with each dispersion a zone of maximum colloidality, above which apparent viscosity decreases with coarser subdivision (about 100 μμ) and below which it also decreases as molecular dimensions are approached (about 5 μμ).

It does not appear possible without more experimental data than have yet been published, to classify colloids strictly according to their consistency. A convenient classification, almost entirely on a physical basis, has been given by Burton [30] and this has been followed in the discussion below.

Colloidal solutions are divided into two main classes, which may be called emulsoids and suspensoids, although various other names are in use. The former are reversible, *i.e.*, they may, like gelatine, be dried and redissolved in water without destroying the colloidal state. In one class of colloids, intermediate between the two main classes, the stability depends upon some emulsoid acting as a "protecting colloid" which seems to prevent the particles of a suspensoid from coalescing into larger masses. For example the eggs or gelatine in ice cream or gum arabic in "gum drops" furnishes the protective colloid.

The suspensoids are non-gelatinizing, *i.e.*, they do not form a solid jelly with water, and (except when accompanied by a protective colloid) may be divided into the following four classes:

1. Irreversible and with low content of disperse phase. This class is represented by soaps and dyes and by Bredig's sols, which are metals brought into the colloidal state by the electric current.

2. In class 2 (and also in class 3) the stability depends upon a trace of salt absorbed by the colloidal particles, as indicated by the fact that coagulation is produced if the salt is removed by dialysis. There is a high content of disperse phase and a precipitate or residue cannot be redissolved and changed back into the colloidal state. Globulin and ferric hydrate belong to this class.

3. "Peptized colloids." Colloids of class 3 may be prepared by the process of peptization, in which a moist coagulum is redissolved. Dialyzed egg albumin and various oxides and sulphides belong to this class.

4. The colloids of class 4, of which Cassius' purple is an example, are composed of reversible particles which are themselves composed of two different kinds of irreversible colloidal particles in definite proportion.

It has been so often shown that the apparent viscosity of emulsoids varies with the rate of shear that there can be no doubt that emulsoids are plastic when of high enough concentration and of sufficient age. Garrett [31] found that the apparent viscosity of gelatine, as measured by the oscillating disk and by the efflux method, in which the rates of shear were probably different, failed to agree, which indicated that the gelatine solution was plastic.

Hatschek [32] found with a rotary viscometer that the deflection was not proportional to the speed, as it is with viscous liquids when there is no turbulence, and that "gum arabic and gelatine sols" had different apparent viscosities at different rates of shear below certain limits. The limitation, "below certain limits," is necessary because it is only at low rates of shear, when the resistance to the yield value is considerable in proportion to that due to $\frac{1}{M}$ that the variation in apparent viscosity is noticeable.[33]

Very little is known concerning which suspensoids are viscous and which plastic. When the content of the disperse phase is low, or it is stated that the viscosity is but slightly greater than that of the dispersion medium, it might be expected that the solution would be truly viscous. On the other hand, where the content of the disperse phase is high, as in class 2, there would be more probability that the solution would be plastic, at least at some concentration.

Garrett's work also indicates that silicic acid, a colloid of class 2, and albumen, one of class 3, are plastic. With silicic acid as with gelatine, the oscillating disk method gave the higher values of the two methods, even when the apparent viscosity of the silicic acid "was not much greater than water." Tests on albumen were made before and after boiling, with results as given in Table II.

TABLE II

Tests by Garrett of the Consistency of Albumen

	Before Boiling	After Boiling
By disk method	.2278	.2032
By efflux method	.1250	.1851

Garrett, who believed his results confirmed the foam cell theory of Quincke,[34] concluded that continued boiling destroys the cells and a solution then behaves like a homogeneous fluid. It would be necessary to determine the yield value and mobility of these colloidal solutions, rather than a single numerical value supposed to represent the "viscosity," in order to determine even roughly the effect of boiling.

Almost every book on colloid chemistry contains the equation, given with slight variations by Einstein [35] and by Hatschek,[36] from which it is supposed to be possible to calculate the viscosity of a suspensoid. It does not apply to an emulsoid because based on the assumption that the particles are rigid spheres.

$$\mu_c = \mu_o(1 + mf) \tag{8}$$

where μ_c = viscosity of the suspensoid
μ_o = viscosity of the medium
f = ratio of aggregate volume of solid particles to total volume of suspensoid.

The coefficient m was first given by Einstein as unity, and afterwards in correspondence with Bancelin [37] he gave it as 2.5 without explanation as to how this value was obtained. Bancelin himself found an experimental value of 2.9. Hatschek at first gave a value for m of 4.5.

Einstein applied his formula to a 1 per cent sugar solution, but found that the increase in viscosity due to the sugar was four times as great as calculated, and concluded that "this result can only be brought into accord with the molecular theory by assuming that the sugar molecule decreases the fluidity of the immediately adjacent water so that a volume of water, about three times the volume of the sugar molecule, is linked to it."

Even more conclusive is the work of Humphrey and Hatschek [38] in showing that Equation (8) is of little practical value because based on the false assumption that Stokes' law of spheres falling through a liquid is applicable. In order to get particles roughly spherical in shape, they used rice starch suspended in a mixture of carbon tetrachloride and toluene. Using a torsional viscometer, it was found that the apparent viscosity increased as the speed decreased, but at any rate of shear the apparent viscosity increased more rapidly than the aggregate volume of the suspended matter. "The general conclusion is that the assumption on which the Einstein-Hatschek formula is based, viz., non-interference between adjoining particles, is not tenable in the case of suspensions containing between 2 and 6 per cent of suspended matter."

It would therefore appear that the consistency of suspensoids is a matter for experiment rather than for mathematical calculation, always remembering also the possibility that such suspensoids may be viscous at some concentrations and plastic at others, that they may change in consistency with time and that they may also change in consistency from a break down in structure due to shearing in the test itself.

Hatschek [39] has proposed as a measure of the rate of shear, when comparing tests made by concentric cylinders and by efflux, the shear gradient, or change in rate of shear between the point where the rate of shear is zero and where it is maximum. It would appear preferable to use the mean rate of shear, since there is not a uniform change from one point to the other. At any rate, while results with rotary and with efflux viscometers may be said to agree satisfactorily when testing truly viscous materials, sufficient data are not available to attempt a reconciliation between the two test methods when applied to plastic materials. First will it be necessary to obtain concordant results, independent of the dimensions of the instrument, something which has not yet been accomplished by any method.

7. SUMMARY

1. Much confusion has resulted in colloidal chemistry from the failure to distinguish between a plastic and a viscous material, as may readily be done by an instrument with which the rate of shear in the material under test may be varied at will.

2. The consistency of a plastic material cannot be expressed by a single numerical value. If the apparatus has been standardized and a standard rate of shear adopted, concordant values of apparent viscosity may be obtained in different laboratories, but two materials which showed the same apparent viscosity on test would not necessarily have the same consistency. The consistency of a plastic material must be expressed by an equation or other means which completely defines the variable relation between rate of flow and the force which produces it.

3. With stiff clays and fats the end effects in efflux instruments are excessive, and no method has yet been found to evaluate or eliminate these effects. Therefore the consistency of such materials cannot be expressed by constants of the material which are independent of the dimensions of the instrument.

4. Emulsoids are plastic, but sufficient information is not available to classify suspensoids according to their consistency.

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18a. See a series of papers in *Jour. Phys. Chem.*, Vol. 29, Oct. (1925).

18b. E. C. Bingham, Colloid Symposium Monograph II, p. 109 (1925).

18c. Wo. Ostwald and others, *Kolloid Zeit.*, Vol. 36, pp. 99, 157, 249, 332, and p. 252 of Zsigmondy-Festschrift (1925).

18d. F. D. Farrow and G. M. Lowe, *Jour. Textile Inst.*, **14**, p. T 414 (1923).

18e. It has been suggested by Dr. H. L. Dryden of the Bureau of Standards that equation (6) might be derived from the assumption that the shearing stress $= [(\mu) \times$ rate of shear $\frac{1}{n}$ and then

$$k = \frac{\pi}{(n+3)\ 2^{2n+3}\ (\mu)} \left(\frac{g}{e}\right)^n d^{\,n+3} \tag{7a}$$

which reduces to Farrow and Lowe's equation when $n =$ unity.

18f. Henry Green, *Proc. A. S. T. M.*, 20, part 2, p. 463 (1920).

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26. W. Clayton, "The Theory of Emulsions and Emulsification," p. 28, 1923.

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32. E. Hatschek, *Trans. Faraday Soc.*, **9**, 91 (1913).

33. The reciprocal of mobility has not been named, although it evidently becomes similar to viscosity as the yield value approaches zero. According to Bingham ("Fluidity and Plasticity," p. 218, 1922) rigidity is the reciprocal of elasticity, and it is incorrect (as in *Proc. A. S. T. M.*, **19**, part 2, 642 (1919)) to use rigidity as the name for the reciprocal of mobility.

34. G. Quincke, *Ann. der Phys.*, **46**, 1025 (1915).

35. A. Einstein, *Ann. der Phys.*, **19**, 289 (1906).

36. E. Hatschek, *Z. Chem. Ind. Kalloid*, **7**, 301 (1910).

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39. E. Hatschek, *Koll. Zeit.*, **13**, 95 (1913).

The Viscosity of Colloidal Solutions

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The changes of viscosity which manifest themselves in ageing gel-forming sols are so striking that it is not surprising they should have attracted the attention of Thomas Graham. In a paper on "The properties of silicic acid and other analogous colloidal substances," published in 1864 in the Journal of the Chemical Society, he writes: "The flow of liquid colloids through a capillary tube is always slow compared with the flow of crystalloid solutions, so that a liquid-transpiration tube may be employed as a colloidoscope." While the statement in its general form can no longer be applied to all the systems which have come to be recognized as colloidal solutions, it is still true of the emulsoid or lyophilic sols with which Graham was chiefly concerned; even the term colloidoscope is still appropriate, since in the majority of cases the results of viscosity measurements are qualitative rather than quantitative, *i.e.,* they offer a delicate means of tracing changes the nature of which is not necessarily unambiguous.

The following pages attempt to give a general view of the present state of theory, and a brief survey of experimental results establishing relations between viscosity and other properties. Experimental methods have received attention only in as far as they have had to be adapted to the special problems encountered in the investigation of disperse systems.

THEORY

The first analytical treatment of the case of an ideal suspension is due to A. Einstein.[1] He assumes the suspended particles to be rigid spheres, having a diameter small in comparison with the distances between the spheres, but large compared with the dimensions and distances of the molecules of the liquid, and from the fundamental equations of hydrodynamics[2] deduces the relation:

$$\eta' = \eta(1 + 2.5f) \qquad (1)$$

in which η' = viscosity of suspension, η = viscosity of dispersion medium, and f is the ratio: aggregate volume of solid particles/volume of suspension.

The viscosity of a suspension accordingly increases in linear ratio with the percentage of suspended solid and is *independent of the degree of dispersity,* since the diameter of the particles does not appear in the equation.

It is at once obvious that experimental verification of Einstein's formula is by no means a simple matter. The ratio f in typical suspensoid sols is of the order 10^{2} to 10^{-4}, so that the differences in viscosity are smaller than the experimental error; in the majority of cases the particles are not spherical, and, lastly, the formula involves a volume relation, while all that is generally known is the weight of disperse phase. It will therefore be sufficient to quote three attempts at verification, made in conditions which conform to some extent with the assumptions made in deducing the formula.

M. Bancelin measured the viscosity of gamboge and mastic suspensions made by Perrin's method,[3] containing microscopic particles of spherical shape. He found the viscosity, for equal values of f, independent of the radius, and linear increase of viscosity with concentration up to 3 per cent, with a proportionality factor of 2.9 instead of 2.5.

A much larger range is covered by S. Odén's measurements on sulphur sols [4] with concentrations up to 40 per cent by weight. Two sols were investigated: one, *A*, having submicroscopic particles about 100 μμ diameter, while the other, *B*, was amicroscopic, the diameter of the particles being estimated at 10 μμ. The particles may reasonably be assumed spherical, but there is some uncertainty regarding their volume. Assuming the density to be 2.0, the *increases in viscosity* (*water* = *1*) for the concentrations investigated are as follows:

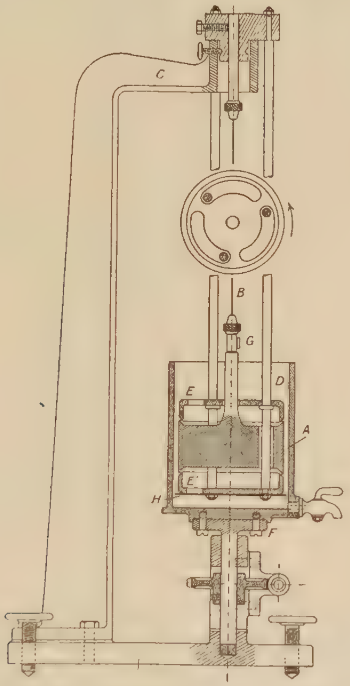

FIG. 1.—Hatschek's modification of Couette's apparatus.

Volume of Disperse Phase, Per Cent	Increase in Viscosity A	B	Ratio B: A
5	0.20	0.30	1.50
10	0.50	0.72	1.44
15	1.00	1.38	1.38
20	1.75	2.63	1.50

In this instance the formula fails in two respects: not only is the increase in viscosity much greater than linear, but the sol with smaller particles (*B*) shows a higher viscosity throughout, for a given concentration, than the coarser sol. The latter discrepancy can be reconciled with the formula if the assumption is made that the particles carry a layer of liquid with them, the thickness of which is the same for both sizes, so that the *effective volume* of the smaller particles is thereby increased much more than that of the larger ones (E. Hatschek[5]). A simple calculation gives the thickness of the layer in the present instance as 0.82 μμ, a value which is quite probable.[6]

Both Bancelin's and Odén's measurements were carried out with the capillary viscometer and involve the assumption, which *a priori* appears quite probable, that suspensions of these types obey Poiseuille's laws or, in other words, that their viscosities are independent of the rate of shear. This point was tested in investigation by Edith Humphrey and E. Hatschek[7] carried out in the latter's modification of Couette's apparatus.

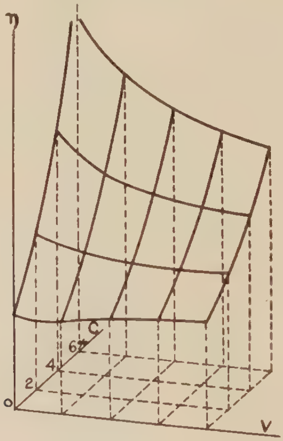

FIG. 2.—Viscosity-shear-concentration surface of rice starch suspension.

> This apparatus (Fig. 1) consists of a hollow cylinder *A*, which is supported by a wire, *B*, from a heavy bracket *C*. The cylinder *A* is open and bevelled at the ends and is coaxial with an outer cylinder *D*. To eliminate the complicated end effect, two short guard cylinders *E* and *E'* nearly closed at one end, are placed opposite the open ends of cylinder *A*, leaving a clearance of about 2 mm. between the bevelled surfaces. The outer cylinder *D* is bolted to a table *F*, which can be rotated by suitable gearing. When the apparatus is filled with liquid and the outer cylinder rotated, a layer 0.5 cm. deep is sheared between the concentric cylinders. The deflection of the suspended cylinder is read by a mirror *G* and telescope. This deflection is proportional to the product: angular velocity × viscosity.

The suspension investigated was one of rice starch in a mixture of toluene and carbon tetrachloride having approximately the same density. The starch granules are not spherical, but polyhedral, and approximately 3 μ diameter.

It was found that the viscosity varied markedly with the rate of shear, so that the complete data have to be expressed by a surface. A perspective view of this, for concentrations up to 6 per cent, is shown in Fig. 2. The sections drawn in full line are viscosity-concentration curves for constant rates of shear, while the dotted sections are viscosity-rate of shear curves, for constant concentrations. The results may be summarized as follows: the viscosity is a function of the rate of shear, and *decreases as the rate of shear increases*, the difference being greater the higher the concentration. For a constant rate of shear, the increase in viscosity with increase in concentration *is more than linear,* and the deviation from the linear law is the greater the higher the rate of shear. If small, approximately linear, portions of the viscosity-concentration curves are considered, the proportionality factor is 15 to 18, instead of 2.5.

On the whole, therefore, a linear formula cannot be considered as anything more than a first approximation. The reasons why it fails have been analyzed exhaustively by M. v. Smoluchowski.[8] The formula is obtained by neglecting the higher terms of a Taylor's series, the first of which neglected terms would already introduce the radius. Furthermore, the electric charge on moving particles produces a pseudo-viscous effect (the existence of which had already been postulated by Wo. Ostwald at an earlier date).[9] Smoluchowski calculates a corrected formula, which contains this effect: as an example of its magnitude it may be mentioned, that for particles of 300 $\mu\mu$ diameter, having a potential difference of 0.038 V. against the water in which they are suspended, the proportionality factor becomes 5 instead of 2.5.

A synthetic treatment of the problem of suspension of rigid spheres has been given by W. R. Hess.[10] He considers flow in a capillary and assumes an ideal arrangement of the spheres, which leaves the whole of the liquid cross section available for the flow. This leads to the formula:

$$\eta' = \frac{\eta}{1-f} \tag{2}$$

in which the symbols have the same meaning as in equation (1). Further consideration shows that the whole cross section left free by the spheres cannot be considered to be flowing, but that there are regions of stationary liquid surrounding the particles. This is taken into account by introducing instead of f a "functional" volume af, the factor a being always > 1, and varying with the experimental conditions. The actual formula thus becomes

$$\eta' = \frac{\eta}{1-af} \tag{3}$$

It will be noticed at once that this equation is *not linear and that, by suitably varying the factor a,* it can be made to fit viscosity-concentration curves of the ordinary type closely. Hess himself tested the formula on suspensions of red blood corpuscles up to 78.8 per cent concentration ($f = 0.788$) and found the value of a to vary between 2.50 and 1.16. The example is not particularly relevant, as red blood corpuscles are far from being either spherical or rigid, and it will be shown below that they can be treated as being almost perfectly deformable.

The viscosity of a system of two liquid or, at any rate, easily deformable phases is of even greater interest than that of a suspension of rigid particles, since such systems of two liquid phases, *i.e.,* emulsions, are known to show the very high viscosities which are also characteristic of emulsoid sols. This problem, in a severely restricted form, has been treated synthetically by E. Hatschek.[11] The percentage of disperse phase is assumed to be so high that the droplets assume polyhedral shape, the ideal form being the rhombododecahedron. If the system is sheared, the polyhedra are deformed, and above a limiting velocity they may not have time to return to their original shape under the influence of the interfacial tension, so that the whole of the shear takes place in the layers of *continuous* phase parallel to the plane of shearing. In that case the viscosity η' of the emulsion is given by the formula:

$$\eta' = \frac{\eta}{1-\sqrt[3]{f}} \tag{4}$$

where η is the viscosity of the continuous phase, and f the ratio: volume of disperse phase/total volume.

It will be noticed that this formula bears a general resemblance to Hess's equation (3), and the two are identical, provided

$$af = \sqrt[3]{f}, \text{ i.e., } a = 1/\sqrt[3]{f^2}$$

It has been shown by Hatschek[12] that this condition is satisfied almost exactly by the suspensions of red blood corpuscles investigated by Hess (*loc. cit.*). It had been shown previously by J. W. Trevan[13] that the viscosity of such suspensions, containing up to 90 per cent could be expressed by the formula (4) with an error of ± 1 per cent, which is of the order of the experimental error.

The evidence afforded by these suspensions is of interest only in so far as it shows that systems the disperse phase of which is readily deformable—although the shape of the particles is far removed from the polyhedral shape assumed to exist initially—exhibit a viscosity-concentration function in good agreement with the formula. The polyhedral structure can be *demonstrated* in the case of emulsions (in the strict sense of the word) only, for which the formula has hardly been tested (E. Hatschek).[14] It is purely hypothetical in emulsoid sols, in which also the difficulty discussed in connection with Einstein's suspension formula, our ignorance of the *volume* of disperse phase, arises in a greatly aggravated form. It is very generally held that the disperse phase in emulsoid sols is hydrated or solvated, but so far no general methods are available for determining the associated solvent or, what is particularly important in the present connection, how solvation varies with temperature and with concentration. The discovery of such a method is the greatest desideratum of colloid chemistry. Failing it, no real test of the formula (4) is possible, and the only thing which has so far been done is to calculate, for a series of viscosity measurements, the *theoretical volumes* of disperse phase and, by comparison with the *weights* of dissolved substance, the solvation factors.

If η' is known, the value of f, the phase volume-ratio, is:

$$f = \left(\frac{\eta' - \eta}{\eta'}\right)^3 \tag{5}$$

and this volume ratio can then be compared with the known concentration by weight. The figures for a number of protein sols are tabulated below:

Sol	Concentration Weight, Per Cent	f Per Cent	Ratio f/C
Sodium caseinate[15]	6.05	58.31	9.638
	7.06	68.63	9.722
	8.49	79.62	9.377
	9.39	87.87	9.358
Euglobulin[16]	10.57	74.85	6.698
	12.32	86.06	6.574
	13.20	90.17	6.415
Pseudoglobulin[16]	14.06	67.20	4.585
	16.43	79.74	4.627
	18.45	87.64	4.499
	20.37	92.42	4.272

It will be noticed that the phase-volume/weight ratio is approximately constant or shows a slight tendency to increase with decreasing concentration, *i.e.*, hydration increases with the latter. This is known to be the case also in true solutions, *e.g.*, of sugar, the evidence being derived from osmotic pressure data.[17] The absolute values of the hydration factors, however, are much higher for the proteins: the ratio f/C is the volume which one gm. of dispersed substance + associated water occupies in the sol: thus one gm. of euglobulin with the water of hydration occupies an average volume of 6.5 c.c. If the degree is expressed *as the number of water molecules associated with one molecule of protein,* the figures become very high, compared with the corresponding ratios in true solutions, *e.g.*, of cane sugar, for which the following figures have been calculated by A. W. Porter:[17]

Grammol. per L. at 0° C.	Molecules of Water per Molecule of Sugar
0.098	53.0
0.192	15.8
0.282	10.3

The hydration rapidly decreases with increasing concentration.

S. Arrhenius[18] has criticized the figures for the proteins given above, partly on the ground that the hydration figures are improbably high, and partly from theoretical considerations leading to the conclusion that hydration ought to be practically constant, *i.e.*, independent of concentration. He applies to the viscosity data for the proteins quoted above, his empirical formula:

$$\log \eta = \theta C \tag{6}$$

where C is the *molecular* concentration. For substances with very high molecular weight this concentration is given with sufficient accuracy by the expression:

$$C = \frac{100p}{100 - (n+1)p} \tag{7}$$

in which p is the number of gm. of solute in 100 gm. of solution, and n the hydration factor, *i.e.*, the number of gm. of solvent associated with one gm. of solute.

When the formula is applied to the viscosities of the protein sols, it fits with remarkable accuracy, both θ and n being constant over a wider range. The hydration factor n comes out as follows:

	n
Sodium caseinate	1.0
Euglobulin	2.2
Pseudoglobulin	1.5

Notwithstanding the high viscosities of the sodium caseinate sols, the hydration factor is the lowest among the proteins quoted, a somewhat surprising result which Arrhenius explains by the dissociation of the caseinate.

In the absence of any independent method of determining hydration the choice between the results deduced from the two formulæ remains open. Both, however, fail when applied to the typical emulsoid sols with very high viscosities, such as rubber in benzene or cellulose nitrate in various solvents. In these systems the viscosity of sols containing one per cent by weight is frequently a hundred, and more, times as high as that of the dispersion medium.[19] If Hatschek's formula (5) is applied to these data, solvation factors of the order 60 to 70 are obtained at low concentrations, which rapidly decrease with rising concentration. If the solvation factors are calculated from Arrhenius's formulas (6) and (7) in some cases factors of the same order are obtained, while in others negative solvation factors are found, which of course have no physical meaning. The problem of finding a rational formula for the viscosity of the typical emulsoid sols is still unsolved.

The problem is still further complicated by the marked variableness of viscosity with rate of shear. Measurements with the most generally used apparatus, the Ostwald viscometer of the type in which a head of the liquid under examination produces the flow, do not directly indicate the existence of this variation, the viscosity-concentration or viscosity-temperature curves are still in general smooth, although to every determination corresponds a different velocity and therefore a different rate of shear. In addition to this, there is in most cases a critical velocity, above which the viscosity appears to be independent of the rate of shear, and this critical velocity is probably exceeded in many cases, especially with narrow capillaries and moderate times of efflux.* When a method is used which permits low and variable rates of shear to be used, the variableness of the viscosity is, however, very easily demonstrated. Such a method is, *e.g.*, that of measuring the logarithmic decrement of the amplitudes of a circular disc oscillating in the liquid, from which the viscosity coefficient can be deduced, which was first applied to emulsoid sols by H. Garrett.[20] He investigated gelatin, albumin and silicic acid sols, with the following results: generally speaking, the viscosities determined with the oscillating disc were *higher* than those obtained by the capillary viscometer, in one case (silicic acid sol containing 3.76 per cent of

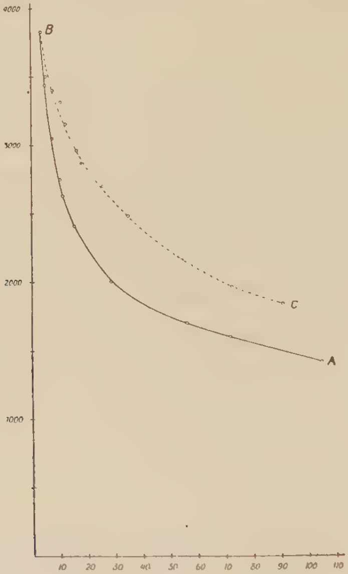

FIG. 3.—Viscosity-shear curves of gelatin sol.

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* The kinetic motion of the dispersed particles in the sol is a factor to be reckoned with. See J. Alexander, this volume, p. 11 *et seq.* J. A.

SiO_2) 2.5 times as high. The viscosity also varied with the amplitude of the oscillations, and furthermore with time. In gelatin sols it increased with time without this change being due to an alteration in the bulk of the sol: if the disc was cleaned and then set in motion again the decrement returned to its original value.

While these experiments prove that the viscosity varies with the rate of shear, they are not easy to interpret, since the rate is not uniform but varies from zero at the center to a maximum at the periphery. The concentric cylinder apparatus is free from these complications and in the modified form described above has been used by Hatschek to measure the viscosity of some gelatin sols at very low rates of shear. In all cases the viscosity *decreased with increasing rate of shear and appeared to tend to a constant value,* which, however, was not reached. The graph of one series of measurements[21] is illustrated in Fig. 3. The ordinates are relative viscosities (water = 1), the abscissæ angular velocities of the rotating cylinder in degrees per second, to which the rate of shear is simply proportional. The sol was a 0.5 per cent gelatin sol 72 hours old. Ten readings were taken with gradually decreasing velocities and then ten with increasing viscosity: there was marked hysteresis, the second curve lying entirely above the first one. The viscosity at the lowest velocity is approximately *two and a half times* as great as that at the highest. The fact that this result was first obtained with decreasing rate of shear, and that the curve for increasing rate lies entirely above the first one, shows conclusively that the effect is not due to the well known lowering of viscosity by continued shearing. The effect of shearing is, however, extremely marked in starch sols, where it outweighs the other factor, as is evident from the graph for a 1 per cent starch sol (Fig. 4) which is plotted in the same way as that for gelatin.

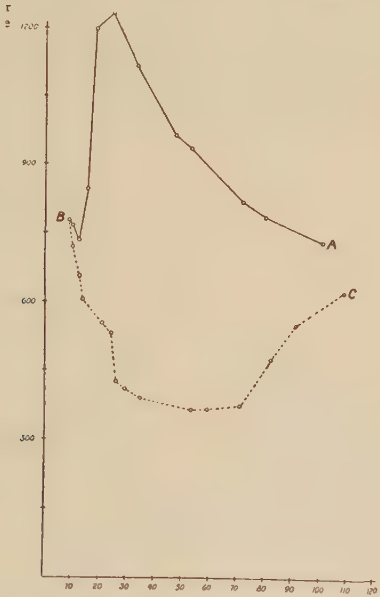

FIG. 4.—Viscosity-shear curve of starch sol, illustrating destructive effect of shearing.

Although the viscosity-shear curves obtained in this investigation appear to tend to a constant value independent of the rate, this value was not actually reached in any series of measurements. If a structure, such as the polyhedral structure postulated by Hatschek, is assumed, the existence of a critical rate of shear, above which the viscosity coefficient is constant, can be deduced theoretically; experimental proof of this critical point has been given by R. W. Hess[22] for blood, serum and a number of emulsoid sols. He used a capillary viscometer with *horizontal* tube, through which the liquid was forced by compressed air, so that the pressure could be adjusted at will. He found that the viscosity was constant only *above a certain pressure, i.e., rate of shear,* but that below this critical pressure it varied and increased with decreasing pressure. Similar results were obtained by E. Rothlin[23] with the same method for serum and for gelatinizing sols like gelatin, agar and ordinary starch, also for albumin; sodium caseinate, gum arabic and soluble starch, however, behaved like normal homogeneous liquids, the viscosity being independent of the pressure. Hess, Rothlin and other observers[24] ascribe the anomaly of the gelatinizing sols to their possessing elasticity of shear, for which there is other evidence, *e.g.,* accidental double refraction during shearing,[25] the elastic limit being so low that above a certain rate of shear the liquid behaves normally. While this explanation is no doubt correct, it cannot be complete, as suspensions of rigid particles have been shown above to show the same variation of viscosity with rate of shear and no evidence of elasticity in such systems is available. An explanation adopted by a number of investigators,[26] which disposes somewhat sweepingly of the whole difficulty, is that these anomalies are due to incipient gelation—which, again, may be the case but also fails to explain the behavior of the starch suspension, in which gel formation is certainly excluded. Even in gelating sols the stage at which incipient gel formation manifests itself has in the majority of cases—been assumed *ad hoc,* since there is no independent evidence of such a change in dilute sols. One of the rare cases, in which the transformation from sol to gel has actually been studied ultramicroscopically therefore deserves special mention: that of the concentrated and aged ferric hydroxide sols investigated by E. Schalek and A. Szegvari.[27] These sols set to gels on addition of electrolyte in suitable concentration, the gels on shaking become liquid and the sols thus re-formed gelate again, the whole process being capable of indefinite repetition. The authors have measured the viscosity change during gelation and, having succeeded by the use of special optical arrangements in resolving the sol in the ultramicroscope, have followed the behavior of the particles during gelation. They find that the particles *do not approach one another* and therefore conclude that the rise in viscosity during gelation is not due to linking but to a change *in their effective volume.*

This assumption is also the only one which explains the variation of viscosity with rate of shear in a suspension of rigid particles, demonstrated by Humphrey and Hatschek (see above). Each particle must be surrounded by a layer of liquid—adsorbed if one likes to call it so—which moves with it and increases its effective volume, and this layer is so labile that it is more and more reduced in thickness as the rate of shear increases. It also takes an appreciable time to build up again, as the shear-viscosity curves exhibit slight, but marked, hysteresis.

It must, in fact, be generally recognized that the viscosities of diphasic systems are governed by *volume relations alone.* Until more is known about the actual volume of disperse phase, whether this be formed by solid particles surrounded by a labile layer or by micellæ containing intra-micellar liquid, a complete rational treatment of the problem appears impossible. An independent method of determining solvation (in its widest sense) is therefore required, as has already been pointed out, but the prospects of such a method being discovered do not appear hopeful.

Experimental Data.

A large number of viscosity measurements, showing the variation with concentration, temperature, age and electrolyte content, are to be found in the literature, the most important of which are given in the bibliography at the end of this chapter. From what has been said above it will be realized that the interpretation of the results in the present stage of our theoretical knowledge is ambiguous, and in many cases has been arbitrary: thus, the decrease in the viscosity of rubber sols on ageing[28] in the light is usually ascribed to "depolymerization," while the increase in viscosity of ageing gelatin or silicic acid sols is accounted for by "incipient gel formation," without much independent evidence for either. Many determinations therefore have a *qualitative* interest only: they indicate the occurrence of a change without furnishing data as to how it is caused. A few examples which, notwithstanding this general difficulty, throw light on points of interest, are therefore all that will be discussed in detail.

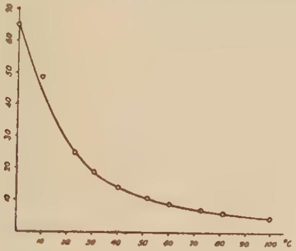

Fig. 5.—Viscosity-temperature curve of sodium caseinate sol.

Temperature coefficient.—The temperature coefficient of viscosity of suspensoid sols is, within the limits of experimental error, that of the dispersion medium, when the concentration of disperse phase is of the usual low order. Very high concentrations are attainable with S. Odén's sulphur sols, and this author[29] has determined the temperature coefficient of viscosity for sols containing from 3.84 to 58.28 per cent of disperse phase by weight, or approximately 1.92 to 29.14 per cent by volume. He finds that $d\eta/dt$ increases with the concentration and decreases with rising temperature.

The temperature coefficient of the viscosity of emulsoid sols is always greater than that of the dispersion medium, and attains extreme values in the sols which form heat-reversible sols, *e.g.*, gelatin or agar in water, cellulose acetate in benzyl alcohol, etc. Even in sols which do not gelate the temperature coefficient is high, as shown, *e.g.*, in the graph Fig. 5, which represents the viscosity-temperature curve of a 9.4 per cent sodium caseinate sol determined by H. Chick and C. J. Martin.[30] The abscissæ are temperatures and the ordinates *relative viscosities referred to water at the same temperatures, i.e.*, viscosity of sol at $n°$/viscosity of water at $n°$. If the temperature coefficients were identical, this relation would give a straight horizontal line; the vast difference in the values of the thermal coefficients shows itself strikingly in the extreme values, the viscosity of the sol at 0° being 64.9 times that of water at 0°, while at 99.6° it is only 4.64 times that of water at this temperature. The authors ascribe the rapid fall in relative viscosity to progressive dehydration of the disperse phase with a consequent decrease in effective volume. It is in agreement with this view that the difference becomes less marked at low concentrations at which the decrease in volume of disperse phase caused by dehydration is less marked; thus a 1.68 per cent sol shows a decrease in viscosity between 17° and 50° which is only 1.18 that of water.

Viscosity in different dispersion media.—It is a well known fact that sols containing the same substance in the same concentration may have widely different viscosities. Opportunities for observing the effect of the dispersion medium arise chiefly in the case of substances which disperse in a number of organic liquids, *e.g.*, the esters of cellulose and india rubber. The table below, which shows the viscosities of sols made from the same brand of nitrocellulose in three different solvents, is taken from a very complete investigation by F. Baker.[31]

Solvent	Concentration Per Cent by Weight	Relative Viscosity (Solvent = 1)
Methyl acetate	0.397	11.7
	0.793	72.1
	1.585	980.0
Ethyl formate	0.358	14.1
	0.717	70.6
	1.439	1050.0
Ethyl acetate	0.384	18.2
	0.7667	175.0
	1.531	3940.0

Incidentally these figures illustrate the enormous viscosities produced by very low concentrations, which are characteristic of many emulsoids with organic dispersion medium. Differences of the same order have been obtained by E. W. J. Mardles[32] for cellulose acetate in different dispersion media.

An attempt to explain the effect of the dispersion medium on the viscosity of rubber sols has been made by F. Kirchof.[33] He gives, among other data, the following relative viscosities for sols containing 3 per cent of rubber in various solvents:

Solvent	Relative Viscosity
Petroleum ether	94.0
Benzene	97.3
Carbon tetrachloride	211.3
Tetrachlorethane	168.0
Pentachlorethane	213.5

The viscosities in the chlorinated hydrocarbons are about twice as high as those in petroleum ether and in benzene. Kirchof coördinates these figures with the data obtained by F. Posnjak[34] for the amounts of different solvents imbibed by rubber during swelling: the volumes of benzene, tetrachlorethane and carbon tetrachloride at equilibrium are in the ratio: 50:60:69. Kirchof assumes that to increased swelling corresponds a higher degree of solvation in the sol, *i.e.*, a relatively larger volume of disperse phase with a corresponding reduction in the volume of "free" dispersion medium.

Viscosity and physical properties of dry colloid.—In view of the comparative ease with which viscosity can be determined, many attempts have been made to coördinate physical properties—some of them not too well defined—of glue and gelatin with the viscosity of their sols [34a] for which the special literature must be consulted. Conditions are, as usual, simpler in non-aqueous systems, and among the first to be investigated were india rubber sols (P. Schidrowitz and H. H. Goldsbrough,[35] van Heurn [36]). Schidrowitz and Goldsbrough showed a distinct parallelism between the viscosity of (raw) rubber sols in benzene and the "nerve" of the material—a somewhat indefinite constant, which may roughly be taken to vary as the elastic modulus. M. Le Blanc and M. Kroeger [37] in a recent investigation deal with rubber vulcanized in the sol by sulphur chloride and find parallelism between the viscosity and the tensile strength of samples of the same rubbers vulcanized cold, while the gelation times of the vulcanized sols increase in inverse order as the tensile strengths.

Probably the most interesting instance of how the viscosity of a sol may be the expression of some deep-seated property of the dry material is to be found in cellulose and nitrocellulose. A large amount of research was directed during the war to the discovery of a method for selecting raw cotton so that, on nitration, a gun cotton with definite properties should result. It was found that the viscosities of sols of the celluloses in cuprammonium solution, and the viscosities of the nitrocelluloses made from them, in a standard dispersion medium like acetone or ether-alcohol, went parallel. R. A. Punter,[38] who gives a summary of the work, states: "The relation between the viscosity of the ultimate nitrocellulose from each cotton and the viscosity of the cellulose from which it was prepared is definite." The conclusion that some element of structure in the original fiber preserves its character after dispersion by cuprammonium on the one hand, and after esterification and dispersion in entirely different media on the other, is irresistible and deserves more attention than it has received so far.

Viscosity and age.—The majority of emulsoid sols exhibit continuous changes in viscosity on ageing. In gelating sols, even in concentrations lower than those necessary for actual gel formation, the viscosity generally increases with time up to a maximum; in other sols, *e.g.*, india rubber sols, the viscosity decreases with time.* A correct interpretation is impossible in the absence of independent methods of determining the degree of solvation of the disperse phase. The effect is also distinctly more specific than the connection between viscosity and other physical properties. A list of papers, not so far referred to, is appended, in which information on this point, and other characteristics of specific sols, will be found.

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The Sol-Gel Transformation and the Properties of Jellies

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A jelly * is described as consisting chiefly of gelatin, having a characteristic soft, stiff, homogeneous consistence and usually semi-transparent, or anything of the consistence of jelly. And, though jellies are not necessarily elastic, without a knowledge of their structure, it is difficult to frame a definition except by reference to gelatin. General acceptance of this substance as typical of the colloid state has necessitated detailed investigation of its properties, in spite of the fact that its chemical constitution remains unknown. Since the foundations of colloid science were laid by Graham, there has been a tendency to regard colloids as substances having properties altogether peculiar. Gradually has it become apparent that the colloid condition is merely a state of matter possessing enormous specific surface. Yet the natural gel-substances, which include gelatin and agar, have been considered essentially different from materials more easily crystallizable.

Of the constitution of jellies very many mutually incompatible theories have been proposed. These fall naturally into three groups: (1) one-phase or molecular systems, (2) two-phase liquid-liquid systems and (3) two-phase liquid-solid systems. To the first class belong Proctor's [1] hypothesis that a jelly is a more or less solid solution of a liquid in the colloid substance, and McBain's [2] view that identical colloidal particles are present in the sol and gel state, which differ only in mechanical properties. Sutherland's [3] conception of chains of molecules belongs to this group. While Hardy,[4] Quincke,[5] Garrett [6] and Wo. Ostwald [7] have suggested that gels are composed of two liquid phases. Theories in these two first classes are unable easily to explain the loss of mobility that occurs during the gelation process, and those in the second group have the additional difficulty [8] that no liquid-liquid system can be imagined which would have the elastic properties of jellies. Nor is there direct evidence for any of these hypotheses.†

The third possibility remains that gels have a solid phase. This idea is the most natural and was the first to be held. It was proposed by Frankenheim in 1835 and revived by K. von Nägeli in 1858, who thought, as appears to be the case, that gels are composed of molecular complexes, or micellæ, with crystalline properties, the water being held by molecular attraction in the interstices within and between the micellæ. Later Bütschli,[9] van Bemmelen,[10] Bachmann,[11] Robertson [12] and Miss Lloyd [13] have preferred the narrower conception, which is not true in every case, that the solid matter forms a framework within the gel. However, assuming that gels contain a solid phase, we have to inquire into the origin of the solid, and why such substances as gelatin

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* Murray's Dictionary.

† S. U. Pickering made solid gel-like emulsions containing over 99% of petroleum and about ½% of soap solution. J. A.
But this is unlike ordinary jellies, both in concentration and method of preparation. S. G. B.

and agar should occur, almost invariably, in the colloid state. The simplest hypothesis[14] that the gel-substance was originally in solution and has crystallized out is sufficient to explain the facts, and, although much further work is needed, covering the whole field of colloid chemistry, the hypothesis promises, eventually, the quantitative explanation of all the properties of colloids.

The theory of colloidal behavior, therefore, must be based on a knowledge of the forces acting on particles in solution. Unfortunately, in current theory these forces have been almost ignored, and a new kinetic theory of solutions is needed before so-called colloid solutions can be understood properly. Preliminary attempts[15] towards a molecular theory of solution have been made. Atoms may be regarded no longer as hard elastic spheres. Instead, we know them to be composed of positive and negative charges of electricity. Accordingly, there must be a residual field of force surrounding each molecule, whereby all molecules attract one another, whether alike or unlike. Larger particles, built up of several molecules, possess smaller stray fields, approximately inversely proportional to the volumes of the particles. To this attraction are due the cohesion, K, and surface tension, S, of substances, and these are related by Edser's[16] equation

$$S = \frac{K\delta}{4}, \tag{i}$$

δ being the nearest distance of approach of two molecules.

The force between two particles may be represented by

$$f = \frac{M_s M_l}{r_{sl}^8}, \tag{ii}$$

where M_s and M_l are the moments of the two particles. Now, in the surfaces of most solids, particles are held so firmly by molecular attraction, that their kinetic and vibrational energy is insufficient to enable them to escape as vapor. If, however, the solid be introduced into a liquid, the conditions are changed. The surface attraction towards the solid will be opposed by an attraction towards the liquid, so that particles of the solid that acquire a certain critical velocity, v, normal to the surface, will be able to escape into the liquid. Of those that so escape, any that come again within the zone of attraction of the solid will be reclaimed, and the solution will increase in concentration of the solid until the number of particles entering and leaving the liquid is equal. It is evident, therefore, that the equilibrium between a solid and its solution is similar to that between a liquid and its saturated vapor.

Investigation shows that the latter equilibrium is determined by the relation

$$\Phi_l = \frac{\Phi_s}{\lambda} e^{\frac{V^2}{\lambda^2 V_{pl}^2}} \tag{iii}$$

where the subscripts s and l refer to the liquid and its vapor, respectively, Φ being the co-volume, V_{pl} Maxwell's most probable speed of the particles in the liquid, and λ the ratio of the most probable speeds in the liquid and vapor states.

The work done by a particle escaping from the liquid into the vapor is

$$W = 3.21 \times 10^{-24} KV \tag{iv}$$

V being the molecular volume in the liquid state. From this the critical speed can be calculated by means of the relation

$$\tfrac{1}{2}mv^2 = W \qquad \text{(v)}$$

where m is the absolute weight of a particle.

By combining equation (v) with that representing the pressure due to given number of particles in motion, the vapor-pressure in atmospheres of a given liquid, at absolute temperature, T, is obtained in the form

$$p = 81.87\,\frac{T\lambda}{\Phi}e^{-\frac{2.414 \times 10^{-8}K}{\lambda^2 T}} \qquad \text{(vi)}$$

To evaluate p we have, if M is the molecular weight, ρ the density, and ρ_m the density near the freezing point:

$$K = \frac{4S}{\delta}$$

$$\delta = \left(\frac{3.24M}{2.016\rho_m}\right)^{1/3} \times 10^{-8}\ cm. \qquad \text{(vii)}$$

$$\Phi = V - \frac{\delta^3}{4} \qquad \text{(viii)}$$

giving

$$p = 81.87\frac{T\lambda}{\Phi_s} = e^{-\frac{9.6565V}{\lambda^2 T\delta'}} \qquad \text{(ix)}$$

where $\delta' = \delta \times 10^8$

The relation between λ and the density of the liquid is given by a smooth curve.

For non-associated liquids, vapor-pressures calculated from (ix) agree remarkably with the observed values, as shown in Table I. If the theoretical and actual values are not the same, association is indicated, and the formula can be used to calculate the degree of polymerization. This is given under A in the Table.

It is hoped that it will be possible similarly to calculate the force to be overcome by a particle escaping into solution and obtain an exact formula for solubility. In the meantime, the force opposing solution may be shown to be proportional to

$$F = \frac{M_s^2}{r_s^8} - \frac{2M_sM_l}{r_{sl}^8} + \frac{M_l^2}{r_l^8}, \qquad \text{(x)}$$

the subscripts s and l referring to solid and liquid respectively. The complete formula would include, in addition, co-volume and density, but this expression is sufficient to give an approximate explanation of all the properties of solutions.

Obviously solubility decreases as F increases, and vice versa. The first term on the right hand side represents the cohesion of the solute particles, the middle term the adhesion of solute and solvent, and the last term the cohesion of the solvent. The following relations are easily deduced:

(1) If the first term is greater than the third, as for solutions of inorganic salts in water, the first term will increase more rapidly than the second, so that F will become greater, and solubility less, as the cohesion of the solute increases.

TABLE I

Substance	Molecular Weight M.	Temperature Centigrade	Density ρ	Molecular Volume V	δ'	Co-volume Φ	Surface-tension S	Association Calculated From Vapor-pressure	Association Calculated By Other Methods	Vapor-pressure Calculated Atmospheres	Vapor-pressure Calculated Mm.	Vapor-pressure Observed Atmospheres	Vapor-pressure Observed Mm.
Ether	74.08	34.8	0.698	106.13	5.277	69.39	15.9	1.00		1.04		1.00	
		20.5	0.758	97.73	5.277	60.99	21.5	1.00			74.0		c. 68
n-Hexane	86.12	20.0	0.660	130.60	5.905	79.10	17.41	1.00			100.0		120
p-Xylene	106.08	136.2	0.757	140.13	5.555	97.28	18.1	1.00		1.00		1.00	
		25.7	0.857	123.68	5.555	80.83	29.1	1.00			14.0		—
Toluene	92.06	109.4	0.780	111.13	5.383	79.12	19.5	1.00		1.32		1.00	
		26.0	0.860	107.05	5.383	68.06	28.4	1.00			48.0		48
Benzene	78.05	80.5	0.810	96.36	4.946	66.09	20.7	1.065		1.00		1.00	
		20.0	0.878	88.90	4.946	58.63	28.7	1.065	1.05 R & S		75.0		75
Acetone	58.05	56.0	0.710	81.76	4.618	57.14	19.4	1.05		1.02		1.00	
		20.0	0.778	74.61	4.618	49.99	21.9	1.27	1.26 R & S		175.0		179
Ethyl acetate	88.06	77.1	0.816	107.90	5.360	69.40	17.2	1.00		0.95		1.00	
		25.1	0.893	98.61	5.360	60.12	22.2	1.43			94.0		95
Pyridine	79.05	114.5	0.882	89.73	4.911	63.12	25.2	1.18		1.00		1.00	
Aniline	93.04	184.0	0.867	107.80	5.253	71.60	24.3	1.30		0.99		1.00	
		43.1	1.000	93.04	5.253	56.80	40.8	1.60	1.35 T		1.0		1
Alcohol	46.05	78.4	0.737	62.48	4.641	37.49	17.0	2.17		1.01		1.00	
		25.0	0.786	58.59	4.641	33.60	21.3	2.46	2.43 R & S		60.0		59
Water	18.02	100.0	0.958	18.80	3.079	11.50	58.92	2.30	2.66 R & S	1.01		1.00	
		20.0	0.998	18.06	3.079	10.76	70.6	2.60	3.44 R & S		16.9		17

(2) For solutions of a given solute in solvents with less cohesion, the second term will increase faster than the third, or the solubility will increase as the cohesion of the solvent increases.

(3) For substances, such as organic compounds and gases, whose cohesion is less than that of the solvent, the middle, or adhesion, term will be greater and increase faster than the first term, so that F will decrease, and solubility increase, as the cohesion of the solute increases. This rule was discovered by Traube, who showed it to be almost universal.

(4) The solubility of a given substance with less cohesion will decrease as the cohesion of the solvent increases.

By the aid of (i), neglecting changes in δ, these rules may be quoted in terms of surface tension, *e.g.*, (1) Solubilities of inorganic salts follow the inverse order of their increase in the surface tension of the solvent. This is the case, as shown in series II below. And (3) Solubilities of organic substances increase as their diminution in the surface tension of the solvent decreases. Many other relations, previously observed though unaccounted for, may be deduced from a consideration of the molecular forces involved, *e.g.*

I. Increases in surface tension, Cohesion pressure, Adhesion.
  (a) $H < Cs < Rb < NH_4 < Li$ (hydrated) $< K < Na < Li$ (dehydrated)
  (b) $C10_4 < CNS < I$
    $C10_3 < NO_3 < Cl$
    $Br < OH < F < SO_4 < CO_3 < MoO_4 < WO_4$

II. Solubility.
  (a) $H > Cs > Rb > NH_4 > Li$ (hydrated) $> K > Na$
  (b) $I > NO_3 > ClO_3 > Br > Cl > OH > SO_4 > CO_3$

III. Molecular volume.
    $I > ClO_3 > No_3 > Br > Cl > OH > F$

IV. Compressibility of solutions.
  (a) $H > NH_4 > Li$ (hyd) $> K > Na$
  (b) $I > NO_3 > Br > Cl > OH > SO_4 > CO_3$

V. Catalysis of the hydrolysis of esters by bases.
  (a) $Cs > Rb > K > Li$
  (b) $I > NO_3 > Br > Cl > Ac$
    etc., etc.

In fact, capacity for hydration, reduction of vapor pressure, depression of the freezing-point, and all properties of solutions for which sufficient determinations are available, are found to follow the same order, and are, therefore, functions of molecular attraction and motion.

As an example of (4) may be quoted the solubilities of CO_2 in various solvents determined by Just[17] and Kunerth.[18] These are given in the last two columns of Table II. The cohesions were calculated from Eder's formula (i) which gives much more accurate values than any other method, the values of δ being multiplied by $A^{1/3}$ to allow for association. It will be seen that ten out of the 17 substances have solvent powers exactly in the inverse order of their cohesion pressures as required by theory. The solubility quoted for m-xylene is probably an experimental error. Homologous considerations show that m-xylene should come above toluene and benzene. A similar case is that of ethyl and methyl alcohols, of which Just has the solvent powers also in the inverse order. The alcohols come altogether out of position. It will be noticed, however, that while Kunerth's figures for other solvents are usually within 2 units of those obtained by Just, the figures for methyl alcohol differ by eleven units. There is obviously some disturbing factor, which may be the presence of a trace of moisture. The remaining exceptions are ethylene di-chloride, nitro-benzene and carbon tetra-chloride. These have densities greater than 1, beyond which the relation is not so simple between λ and density, and the formula (x) is not a complete guide to the order of solubility.

TABLE II

Substance	$\delta \times 10^8$	A	S	$K \times 10^{-9}$	Solubility of CO_2 in Mol-fractions × 10^4 at 20° Just	Kunerth
Acetone	4.679	1.27	23.1	1.81	209	211
Pyridine	4.911	1.18	25.2	1.93	129	129
Ethylene chloride	4.959	1.06?	31.4	2.48	125	—
Chloroform	4.994	1.03	26.9	2.01	123	121
Acetic acid	4.508	1.92	27.6	2.15	121	124
Nitro benzene	5.473	1.1?	41.98	2.67	113	—
Toluene	5.383	1.01	29.1	2.16	107	—
m-Xylene	5.55?	1.00	28.5	2.08	102	—
Carbon tetra-chloride	5.313	1.01	26.0	1.96	100	—
Benzene	5.192	1.065	28.5	2.16	91	—
Propyl alcohol	4.798	2.25	23.3	1.48	77	—
Ethyl alcohol	4.641	2.43	22.03	1.41	70	69
Methyl alcohol	3.892	2.89	22.6	1.63	71	60
o-Toludine	5.517	1.03?	37.8	2.72	66	—
Aniline	5.253	1.60	43.2	2.73	55	53
Carbon di-sulphide	4.618	1.07	33.58	2.94	22	—
Water	3.079	3.44	72.53	6.24	7	7

Consideration of molecular attraction allows the deduction also of a quantitative expression for the increased depressions of the freezing points of aqueous solutions of inorganic salts. The normal depression, D, by a solute that does not appreciably affect the cohesion pressure of the solvent is

$$D = \frac{0.02T^2}{L}$$

where L is the latent heat of the solvent. Now the cohesions of inorganic salts are much greater than that of water. For instance, Edser gives $K = 11.48$ for sodium chloride at 802.6° as compared with 6.38 for water at 100° or the value would be greater at room temperature. Consequently, dissolved salts increase the surface tension and cohesion pressure of water. But increased pressure depresses the freezing point of water by 8.5° per 1000 atmospheres. There is no escape from the conclusion, therefore, that salts must depress the freezing point of water more than substances which affect its cohesion inappreciably.

If the exact degree of association of water were known, the formula (i) would give the relation between the cohesion of dilute solutions and their surface tension. Assuming Ramsay and Shields earlier figures for water, $A = 3.44$, we obtain

$$K = 84.7S.$$

Walden[19] deduced the relation

$$K = 75.3S. \tag{xi}$$

the latter expression using the additional depression of the freezing point by the increased cohesion,[15] is

$$\Delta D = \frac{\Delta S \times 75.3 \times 8.5}{1000}$$

$$= 0.64\Delta S \tag{xii}$$

where ΔS is the observed increase in the surface tension. Table III shows how nearly the observed increases in the depression of the freezing point, ΔD, compare with the values of $0.64\Delta S$.

When, therefore, lyotrope series, similar to those mentioned above, are encountered in colloid chemistry, it may be expected that the effects are due to the fields of force surrounding the particles. It follows also that lyophile substances have less attraction for the dispersion medium than lyophobe, and also that every substance must have a definite solubility, however small, in a given solvent with which it does not combine chemically.

If the solid phase be removed[20] from contact with a hot solution, statistical equilibrium, between the particles leaving and returning to the solid, will be possible no longer. Diminishing kinetic energy of the particles, with falling temperature, will allow their aggregation, and the solution will become supersaturated. Permanent association of colliding solute-particles will occur when their kinetic energy falls below a certain limiting value. With dropping temperature, the aggregates will grow, until they have reached such a size that the force of gravity dominates their kinetic energy and causes them to subside. On these, the excess of solid will be deposited, and the statistical equilibrium, between solid and solution, re-established. That is to say, the cooling solution will pass through a metastable stage before spontaneous crystallization commences.

Von Weimarn's[21] experiments show that the form, in which a given substance will be precipitated, is determined by the value of the coefficient, N, in the formula

$$N = U \cdot \frac{P}{L} \tag{xiii}$$

where L is the solubility of the given substance, P the supersaturation, and U is an unknown function that varies in the same sense as the actual size of the particles in solution and the viscosity of the reaction medium, or, probably, inversely as the diffusion coefficient.* As N increases, the precipitate passes through stages in which it appears as: (1) large complete crystals in several years, (2) smaller crystals in a short time, (3) growth-figures or needles, (4) amorphous precipitates frequently containing microscopic spherites, and (5) as a gel which cannot be resolved by the microscope. The formula is not exact. It is being investigated further. However, the expression is very useful in showing how to vary the grain size of a given material. The colloid condition results when N is extremely great. If this be due to a very small value of L, and P be also small, a sol will be produced; if P be great a gel will be formed. The value of P is much affected by the metastable limit, or the velocity of crystallization. If crystallization become

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* See paper by P. P. von Weimarn, this volume. J. A.

TABLE III

Grams / 100 C.C.	G. Moles / Litre	Observed Depression D	Normal Depression	Increase ΔD	Surface Tension S	Increase ΔS	Ratio $\frac{\Delta D}{\Delta S}$	Increase of Surface Tension × 0.64
Sodium Nitrate.								
0.43	0.05	0.17°	0.09°	0.08°	74.23	0.13	0.61	0.08
1.71	0.20	0.67	0.37	0.30	74.57	0.47	0.62	0.30
Potassium Nitrate.								
2.02	0.20	0.64°	0.37°	0.28°	74.52	0.42	0.64	0.27
2.53	0.25	0.77	0.47	0.30	74.57	0.47	0.65	0.30
5.06	0.50	1.47	0.93	0.54	74.86	0.76	0.73	0.49
7.59	0.75	2.11	1.40	0.71	75.04	0.94	0.75	0.60
10.12	1.00	2.66	1.86	0.80	75.22	1.12	0.71	0.72
Sodium Sulphate.								
1.42	0.10	0.43°	0.19°	0.24°	74.40*	0.30	0.80	0.19
2.84	0.20	0.81	0.37	0.44	74.74	0.64	0.69	0.41
4.27	0.30	1.16	0.56	0.60	75.06	0.96	0.62	0.61
7.11	0.50	1.84	0.93	0.91	75.69	1.59	0.57	1.01
Potassium Sulphate.								
0.87	0.05	0.23°	0.09°	0.14°	74.32	0.22	0.64	0.14
1.74	1.10	0.43	0.19	0.24	74.50	0.40	0.60	0.26
3.49	0.20	0.81	0.37	0.44	74.80	0.70	0.63	0.45
7.75	0.44	1.66	0.83	0.83	75.30	1.20	0.69	0.77
Sodium Carbonate.								
0.21	0.02	0.10°	0.04°	0.06°	74.19	0.09	0.69	0.06
0.53	0.05	0.23	0.09	0.14	74.32	0.22	0.63	0.14
1.06	0.10	0.44	0.19	0.25	74.50	0.40	0.64	0.26
2.12	0.20	0.83	0.37	0.46	74.83	0.73	0.63	0.47
5.31	0.50	1.88	0.93	0.95	75.57	1.47	0.65	0.94
Potassium Carbonate.								
0.14	0.01	0.05°	0.02°	0.03°	74.15	0.05	0.64	0.03
0.28	0.02	0.10	0.04	0.06	74.18	0.08	0.75	0.06
0.69	0.05	0.23	0.09	0.14	74.28	0.18	0.79	0.12
1.38	0.10	0.45	0.19	0.26	74.48	0.38	0.68	0.24
2.77	0.20	0.88	0.37	0.51	74.89	0.79	0.64	0.51
Sodium Chloride.								
0.63	0.11	0.38°	0.21°	0.17°	74.32	0.20	0.85	0.13
1.36	0.23	0.80	0.43	0.37	74.54	0.42	0.88	0.27
2.51	0.43	1.45	0.80	0.65	74.91	0.79	0.82	0.51
4.10	0.70	2.40	1.30	1.10	75.40	1.28	0.86	0.82
Potassium Chloride.								
1.56	0.21	0.71°	0.39°	0.32°	74.40	0.38	0.80	0.24
3.10	0.42	1.40	0.78	0.62	74.70	0.68	0.90	0.44
5.60	0.75	2.53	1.39	1.14	75.10	0.98	1.16	0.74

* These figures were calculated from the two sets of determinations at different temperatures. This is a further proof that the properties of solutions are the result of the molecular forces involved.

instantaneous, no further increase in concentration of the reagents can increase *P*. Sometimes the metastable limit can be increased enormously by addition of suitable substances, many having polyvalent radicles. Citric acid has this effect on the precipitation of silver chromate.[22] These considerations allow the explanation of all the properties of jellies.

The literature of organic chemistry abounds in descriptions of definite substances which occur in the gel form. Frequently these have been obtained, also, as well defined crystals. The following examples are taken at random. The sodium salt of acrylic acid[23] occurs as microscopic lenticular needles. The boiling saturated solution sets on cooling to a jelly which shows no structure under the microscope. Glycyrrhizic acid[24] crystallizes from alcohol as light yellow glistening leaflets, which are better formed the slower the crystallization. It is little soluble in cold water, easily soluble in hot, and the solution forms, on cooling, a light wine-colored jelly. Camphorylphenylthiosemicarbazide[25] occurs as a fine powder composed of crystalline needles. It is slightly soluble in alcohol and toluene in the cold, much more on heating. Rapid cooling of the hot solution, or pouring the alcoholic solution into petroleum, produces a clear elastic jelly. Di-benzoyl cystine gel is formed when 0.2 g of the substance is dissolved in 5 c.c. of hot alcohol, mixed with 95 c.c. boiling water, and allowed to cool. The clear jelly resembles 1 per cent agar gel. The author has proved that the jelly is formed when a saturated solution of the cystine in boiling water is allowed to cool. Pure boiling water takes up even less of the substance than when alcohol is present. These and similar examples are explained by von Weimarn's formula. Gelatin is not an exception. The solubility in water of dry ashless gelatin, purified by electrolysis, is 0.12 gram per 100 c.c. at room temperature. The solubility increases rapidly with rising temperature. When solutions, only slightly supersaturated at a given temperature, are quickly boiled, sealed in tubes and allowed to stand at that temperature in a thermostat, the solutions do not set to a jelly. Instead, they become opalescent, and the excess of gelatin separates very gradually. At room temperature a 0.12 per cent solution remains perfectly clear, a 0.13 per cent solution is metastable and develops a permanent clear bluish opalescence. When the liquid contains 0.135 per cent, or more, of gelatin, the excess is precipitated and, as long as the supersaturation is not great, the volume of the precipitate is exactly proportional to the excess concentration. At 0.7 per cent the precipitate fills the solution, and the liquid sets to a just coherent jelly. Water stirred with gelatin takes up 0.114 g. According to experiments in progress at higher temperatures, the concentration of the liquid above the precipitate agrees with the solubility at each temperature. Similar properties are exhibited by good commercial gelatin.

The molecular weight of gelatin is not known. It has been estimated by various observers at from 10,000 to 25,000 or more. It is probably about 20,000. A molecular weight of half this value would correspond to molecules of colloid size, 1.75 μμ in diameter, having an extremely small diffusion coefficient and velocity of crystallization. The slow velocity of crystallization is the reason that hot concentrated solutions set to jellies on cooling. As the temperature falls, they become more and more supersaturated and the particles increasingly aggregated, giving large values of P and U in (xiii), while the solubility, L, decreases. When spontaneous crystallization ensues, the value of N has become very great and corresponds to the colloid state. In accordance with (xiii), the grain size of the jelly increases continuously with diminishing excess concentration. Six per cent gels,[26] from which the liquid has been expressed, cannot be resolved even by the ultramicroscope. At lower concentrations a globulitic structure becomes apparent, and, as the grains increase in size, the jelly becomes opalescent and then white and opaque. When the concentration falls to 0.4 per cent,[27] the ordinary microscope shows the white gelatinous precipitate to be composed of a multitude of particles like grains of sand, hardly visible separately, with a few larger spherical particles or spherites. At 0.2 per cent the granular appearance is very marked and a number of spherites can be distinguished separately. The continuous increase in grain size is confirmed by application of Stokes' law to the rate of subsidence of the precipitate. The particles fall freely for from a few hours to 30 days, according to the concentration, then the precipitate coalesces to a continuous jelly that shrinks gradually for a long time. Dialyzed agar behaves in the same way, and silicic acid gels show ultramicroscopic granular structure.

These experiments demonstrate that in the process of setting there is actual separation of solid gelatin. If a solution contain more gelatin than corresponds to its solubility under the conditions of the experiment, the excess will be deposited slowly. The gelatin molecules will aggregate in the process of precipitation, and the properties of the liquid will be affected by the presence of these aggregates. For example, at temperatures below about 27° the viscosity[28] of 2 per cent gelatin of p_H 2.7 increases rapidly on standing, owing to the formation of solid micellæ that occlude large quantities of water, controlled by the Donnan equilibrium. At higher temperatures the viscosity is normal and decreases slowly with rise of temperature. In albumin solutions at ordinary temperatures solid particles are lacking, but, if the p_H be below 1.0 and the temperature higher, albumin solutions, also, tend to gelate, solid micellæ are formed, and then the viscosity is of the same order as that of gelatin solutions.

It follows that the terms "melting point" and "setting point" have no exact meaning as usually applied to gelatin jellies and solutions. The solubility of ashless gelatin at 28.35° is 1.15 per cent. A jelly of this concentration will just dissolve completely if maintained at 28.35°. If kept at a lower temperature, an amount of gelatin, corresponding to its solubility at that temperature, will go into solution gradually, or the excess will be deposited, as the case may be. But if, as usually happens, the jelly be warmed until it melts, it will not do so until the temperature has had time to rise considerably above 28.35°, on account of the slow velocity of solution. Conversely, if a warm 1.15 per cent solution be cooled, the liquid will not set until the temperature has fallen much below 28.35 per cent, or, actually, not until it has remained for some time at room temperature. The observed melting and setting points depend on the rate of heating or cooling. Moreover, the grain size of the jelly is affected by the temperature at which the bulk of the excess gelatin is precipitated. When a more exact expression for the grain size has been found, it should be possible to deduce the relations between the excess concentration, and the elasticity, vapor pressure and other properties of jellies.

Gelatin and agar jellies are remarkable for their stability. This is due to the extremely slow velocity of crystallization. Most substances that can be obtained in the gel form, including the soaps, rapidly develop micro- or macroscopic crystals. However, old silicic acid gels show crystalline spherites, and clear gelatin jellies do very gradually become opalescent and develop very tiny microscopic particles. Probably gelatin jellies undergo extremely slow but continual re-crystallization, whereby the larger particles are continually growing at the expense of the smaller ones. When, therefore, a rectangular prism of jelly is bent between three stops and left for five days in a moist atmosphere, the particles of the jelly become fixed in their distorted positions and probably by further gradual separation of solid gelatin, so that when the jelly is removed from the stops it remains bent, and by recrystallization polarized light reveals still the optical anisotropy due to distortion.[29]

Von Weimarn's theory may be applied to obtain the gelatin particles of larger size. For this purpose N must be reduced as much as possible, which can be done by avoiding supersaturation and increasing the solubility. As the presence of traces of salts increases the solubility of gelatin, commercial brands crystallize more readily than pure gelatin. However, the purest ashless gelatin yields spherites up to about 3 μ by spontaneous evaporation at 35° in an air bath. A white gelatinous precipitate forms on the base of the crystallizing dish, or on cover glasses resting thereon. After from ten days to two weeks microscopical examination with a 1/12 objective shows the precipitate to consist of a mass of spherites mostly between 0.8 and 1.5 μ with a few larger ones. All glow distinctly between crossed nicols, some showing shadow crosses, thus proving their crystalline nature. In the presence of 0.1 per cent mercury chloride the spherites can be obtained up to 6 μ or more, see Figs. 1 and 2.

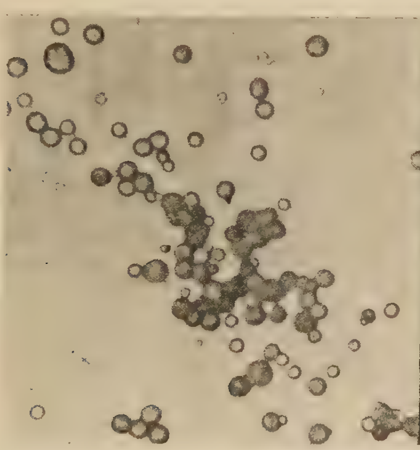

FIG. 1.—Gelatin spherites with $HgCl_2$. × 1400.

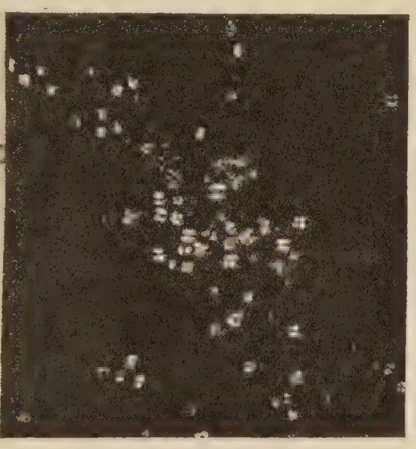

FIG. 2.—The same between crossed nicols. × 1400.

It may be concluded that gelatin, agar and silicic acid jellies are granular in structure. This explains the lenticular form of gas bubbles generated in these gels. The structure of jellies of other substances varies according to their crystalline habit. Barratt[30] found indications of a fibrillar structure in fibrinogen gels. Soap jellies, like those of gelatin may be either transparent or opaque, the former having smaller ultimate particles. Even in these, long filaments are visible ultramicroscopically.[31] In the opaque jellies the crystalline structure may be microscopic, and according to (xiii), with decrease of concentration, the fibrils and spherites increase in size. Fischer[32] has determined the smallest concentrations of a large number of pure soaps that will set to a coherent jelly. For sodium oleate and palmitate these are 23.3 and 1.4 per cent, respectively, the corresponding solubilities being 5.0 and 0.2 per cent. The lowest concentration of gelatin that will set at room temperature is 0.7. This gives $\frac{N}{U}$ in (xiii) equal to $\frac{0.7-0.12}{0.12}$, or 4.8. The concentrations of sodium oleate and palmitate that would give the same value of

$\frac{N}{U}$ are 29 and 1.2. These are remarkably near Fischer's experimental figures, and indicate that U has much the same value for these soaps as for gelatin. Soaps of heavier metals, like lead, have too great a velocity of crystallization to allow the accumulation of sufficient excess concentration during cooling to form a jelly, therefore the excess separates out, as formed, in the state of an amorphous precipitate. That the gelation of organosols of cellulose acetate is akin to crystallization is indicated by the variation of the Tyndall effect[33] and viscosity.

Solubility determinations promise to explain many problems of colloid chemistry hitherto obscure. The optical levo-rotation of a gelatin solution remains nearly constant at temperatures above that at which the solution is saturated. At lower temperatures rotation gradually increases to a constant value.[34] This must be due to separation of solid gelatin. The viscosity of potassium oleate[35] is 1.19 at a concentration of $\frac{N}{20}$. It increases at first slowly with rise in concentration. At $\frac{N}{5}$ it is 1.87. Suddenly the viscosity begins to increase enormously. At 0.4 N it has become 8.02 and rises to 1573 for 0.6 N. Probably the explanation is the same as for gelatin: the solubility of potassium oleate is probably less than 0.4 N, and micellæ begin to be formed in the supersaturated solution.

The influence of salts on the solubility of gelatin would repay further investigation. As gelatin reduces the surface tension of water, its molecular field is probably less than that of water. Adsorption of salts by gelatin particles would produce aggregates with greater residual field of force nearer to that of water. Therefore, smaller concentrations of salts would increase the solubility of gelatin, while larger concentrations would decrease it, because the cohesion pressure of the salt solution increases more rapidly than the amount of adsorbed salt. The maximum solubility is reached more slowly and becomes greater as the cohesion pressure of the salt diminishes, or as its solubility increases. Sodium sulphate[36] decreases the solution time of 0.8 g. of gelatin in 100 c.c. of water, or increases its solubility to a maximum at $\frac{M}{32}$. The greatest effect of sodium chloride has not been reached at 2 M. The smallest concentrations that precipitate 0.8 per cent gelatin solutions are $\frac{3}{4}$ M for sodium sulphate and 3 M for potassium chloride. The effects follow the lyotrope series. Peptization and coagulation, flocculation and deflocculation are to be explained in the same way. The temperature[37] of setting of gelatin depends on the solubility, and is affected by salts in the same way; so are, also, the time of gelation[38] and the rate of increase of viscosity.[39] The more soluble salts depress the gelation temperature, sufficient concentrations of less soluble salts raise it. Small additions of alcohol[36] to warm 1 per cent gelatin solutions, which are not saturated at temperatures above about 26° or 27°, increase the large amounts of salt solutions required to salt out the gelatin. But, when more than a certain quantity of alcohol has been added, the solutions become opalescent and very small amounts of salts are sufficient to cause precipitation. The explanation is, probably, that the solubility of gelatin in water is first increased and then diminished by addition of alcohol. When sufficient alcohol has been added, the gelatin begins to be precipitated, as shown by the opalescence, and the suspension, or suspensoid sol, of gelatin shows the usual sensitiveness to salts. Such questions can be settled only by determination of the solubility of the substance concerned under the conditions of the experiment.

Gels may, therefore, be defined as two-phase liquid-solid systems, comprising innumerable submicroscopic crystalline aggregates, in and around which, the mother liquid, from which the solid disperse phase has crystallized, is held by molecular and capillary forces. In such a two-phase system the liquid exists in three states, the effects of which have been verified experimentally:[40] (1) free liquid contained in larger cavities, (2) liquid retained in the capillary pores between the micellæ, and (3) liquid absorbed in thin skins at the surfaces of the micellæ. The vapor pressure of the system will be less than that of the free liquid. This is the explanation[41] of van Bemmelen's[42] curious hysteresis cycle. With progressive dehydration, the gel decreases in volume and the gel capillaries develop menisci, concave to the vapor phase, with increasing curvature and diminishing vapor pressure. At the commencement of the hysteresis cycle, the radii of the liquid menisci have reached their lowest value, approximately equal to those of the capillaries. They exert a maximum pull on the liquid and the gel as a whole is compressed. The tension causes rupture of the liquid in the interior and an opaque appearance, due to innumerable gas bubbles larger than the interstices between the micellæ. When the emptying of the capillaries is complete, the bubbles have coalesced, and the opaqueness has disappeared. During reimbibition, the un-wetted walls develop liquid menisci with greater radii, higher vapor pressure, smaller pull on the gel and larger water uptake. Silicic acid, charcoal, permitite and porous bodies generally exhibit such variations in vapor pressure according to the liquid content. Gelatin hydro-gels behave rather differently on account of the solubility of gelatin in water, but the water can be replaced[43] gradually by alcohol, and subsequently by benzene and other liquids, which show the hysteresis cycle. From the vapor pressures, the size of the capillaries can be calculated. For silicic acid[44] they vary from 5 to 10 μμ in diameter and for 10 per cent gelatin[43] from 8 to 27 μμ. The diameters of the micellæ would be rather larger than those of the capillary pores between. It is interesting to compare these figures with those indicated by von Weimarn's theory. The rate of subsidence and microscopic appearance of gelatin particles, in the precipitate from a 0.2 per cent solution, agree in fixing the size of the grains at about 0.09 μ. The corresponding value of $\frac{N}{U}$ in $\frac{0.2-0.12}{0.12}=0.67$. For a 10 per cent gel, $\frac{N}{U}$ would be about 120 times as great. Now experiments indicate that N may be nearly a linear function of the reciprocal of the diameter of the particles. If this were exactly true, the particles in a 10 per cent gel, setting at room temperature, would be only 0.8 μμ in diameter. But the solution sets at a higher temperature, so that L would be greater and the particles bigger. The vapor pressure shows that they are 10 to 34 times as large. If, however, gelatin molecules are 1.75 μμ, or more, in diameter, the micellæ cannot contain many molecules, so that there is a large element of truth in theories that jellies are one-phase molecular systems, although a solid-liquid system cannot be so described with accuracy. Also, it is apparent why gelatin gives no interference with mono-chromatic X-rays.

Owing to the small size of the grains, appreciable portions of both solid and liquid exist in the surface skins bounding the two phases, and both experience cohesion pressures intermediate between those of the free substances.

In consequence, the volume of the gel is less than that of the free constituents.[45] When the air-dry gelatin is placed in water, some of the smaller particles dissolve, and the water is attracted into the pores between the particles, causing the gelatin to swell. The swelling does not proceed indefinitely. It is resisted by a force that may reside in the surface of the small particles of the jelly, or be due to their aggregation. With particles so small, it is difficult to distinguish between cohesion and crystalline continuity. The amount of water [46, 47] taken up depends on the previous history of the gel and may amount to as much as 14 times the mass of the gelatin. If sufficient water were added, the whole of a gelatin gel would dissolve gradually, just as a soap jelly slowly disperses in water. The total volume [48] of gel and water after swelling (*e.g.* 1 gram of gum tragacanth in 50 c.c.) may be 2 per cent less than before. The heat [49] evolved by the contraction is 5.7 cal. per gram. However, air-dry gelatin still contains 15 to 16 per cent of water that can be driven off by heating for 18 hours at 110°. The contractions and pressures involved in the retention of this water are much greater. The heat of swelling of dry gelatin is 33.25[50] cal. per gram, that of starch 30 cal. However, the loss of the last traces of water appears to be accompanied by a change in the gelatin, which may be related to that produced in its dehydration by alcohol. A sample of air-dry Nelson's "Crystal" leaf gelatin of density 1.333 in vacuo at 15°, containing 16.53 per cent of moisture, lost only 14.59 per cent by drying over sulphuric acid for a year, retaining 1.94 per cent. The rate of loss of water is shown in Table IV. The gelatin, dried by heating, swells in water, but does not melt in boiling water. The solubility of this heat-dried gelatin at 100°, determined by boiling with water for some time and evaporating the solution, is 0.12 per cent. This is remarkable as compared with the large amount of air-dry gelatin that will go into solution at 100°. Yet this dilute solution becomes gelatinous on standing overnight.

TABLE IV

Days	Moisture Lost Per Cent	Moisture Retained Per Cent
0	0.00	16.53
3	3.55	12.98
5	4.41	14.12
22	8.12	8.41
45	9.81	6.72
1 year	14.59	1.94

The enormous pressures required to squeeze out the water from jellies also indicate the magnitude of the forces involved in swelling. Laminaria requires a pressure of 41 atmospheres [51] to reduce the water content to about 33 per cent of the dry gel. Very much greater pressures would be necessary to remove the remaining water. The contraction, assumed to be confined to the water, involved in its absorption by starch, was calculated by the author from Rodewald's [52] observations, as shown in the fourth column of Table V. It will be noted that up to about 9.8 per cent of water the contraction is practically constant. The contraction of water subsequently absorbed is much less. Generally the water alone is assumed to be concerned in the contraction observed in the total volume of gel and water. If, however, the liquid, adsorbed at the surfaces of the gel particles, be under a greater pressure than the free liquid, the solid gel substance in the thin layer adjacent must be under a less pressure than in the free state, or vice versa. Therefore, the total contrac-

TABLE V

100 G. Starch Dried Over H_2SO_4 Containing Water	Specific Volume	Vol. of Absorbed Water in C.C.	Vol. of 1 G. Water in C.C.	Vol. of 1 G. Additional Water After Subtracting Vol. (= 3.01 C.C.) of First 9.8 G.
0.00	0.72585	—	—	—
1.17	0.72124	0.38	0.33	—
2.69	0.71319	0.78	0.29	—
5.02	0.70486	1.54	0.31	—
7.40	0.69881	2.67	0.36	—
9.70	0.69344	2.79	0.29	—
13.41	0.68727	6.60	0.49	0.91
14.95	0.68555	8.22	0.55	1.01
19.24	0.68111	9.51	0.49	0.68

tion is the resultant of a contraction in one phase and a smaller expansion in the other phase. The pressures required to produce the water contraction, given in the table above, would amount to 8.6×10^4 atmospheres, and the heat evolved would be 120 cal. per gram. But some heat is absorbed in the expansion of the other phase, so that the actual heat of swelling is less.

The properties of gelatin jellies are affected characteristically by the presence of tough skins formed by surface evaporation, the particles in the surface becoming felted and cemented together by deposition of fresh solid. The skin is very noticeable if it is attempted to cut, with a blunt knife or spatula, a jelly that has been exposed to the air for two or three days. Gelatin cylinders, hung in a moist chamber to prevent toughening of the skin, become pear shaped, indicating that their viscosity is not infinite. Some soap jellies easily assume the shape of the containing vessel. When suddenly heated, so as not to melt the skin, gelatin cylinders and prisms contract in the direction of their greatest length owing to the constraint to expansion imposed by the skin. The skins of agar jellies are much less tough, and the jellies do not exhibit this so-called thermal anomaly.

The general conclusion appears to be that the reversible sol-gel transformation is a problem in solutions, and that many colloid phenomena at present obscure will be explained by determinations of solubility.

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The Problem of Gel Structure

By Dorothy Jordan Lloyd, London

The colloidal condition, the "gel," is one which it is easier to recognize than to define, and even recognition is confused by the fact that the limits between gel and sol, on the one hand, and gel and what may be termed curd, on the other, are not precise, but consist of a gradual change. For this reason some workers classify as "gels" systems which others exclude. Only one rule seems to hold for all gels, and that is that they must be built up from two components, one of which is a liquid at the temperature under consideration, and the other of which, the gelling substance proper, often spoken of as the gelator, is a solid. The gel itself has the mechanical properties of a solid, *i.e.,* it can maintain its form under the stress of its own weight, and under any mechanical stress it shows the phenomenon of strain. But it differs from a solid in other important respects, namely (1) that many substances which are soluble in the liquid component can diffuse through the gel with a velocity differing but little from their velocity of diffusion in the simple solvent; * and (2) that chemical reactions can also occur in gels at velocities which are almost unaffected by the gel condition. A final generalization is that a gel is a body transparent to the naked eye, though showing the "Tyndall cone" effect under lateral illumination. Cloudiness or turbidity in gels, when viewed by transmitted light, does of course occur, and even commonly, but the cloudiness is not usually due to an essential part of the structure. It may be due to an abnormally coarse structure, as in Hardy's (1900, 2) gelatin-alcohol-water systems, and the gel of azo-methine in carbon bisulphide (Hardy, 1912), but is more frequently evidence that the system is unstable and that the gelling substance is separating out, as in isoelectric gelatin in water (Jordan Lloyd, 1920, 2; Smith, 1921; Bradford, 1921; Field, 1921; Callon, 1925), soap curds in water (Laing and McBain, 1920), dibenzoyl-l-cystine in water and alcohol (Gortner and Hoffman, 1921), or in water (Wolf and Rideal, 1922). In a few cases turbidity is due to the presence of impurities, as in the gel of commercial agar in water where it is due to the inclusion of proteins, and when these are removed the gel becomes clear.

Von Weimarn (1907), who has made aquagels from numerous inorganic salts such as barium sulphate, manganous cyanide, strontium cyanide, green chrome alum, etc., etc., uses transparency as a criterion of the gel state. To systems which have become cloudy by the separation of the gelator as ultra-microscopic or microscopic crystals, he gives the name "pseudo-gels." This would seem to correspond to McBain's use of the term "curd" for the cloudy gel in the system soap-water. The dividing line between "gels" and "pseudo-gels" has been the subject of a certain amount of controversy.

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* This is not true of concentrated gels. J. A.

CLASSIFICATION

Gels have been classified as heat-reversible and non-heat-reversible (Hardy, 1899, 2; 1900, 2), and as elastic and rigid (Freundlich, 1922). The two methods of classification lead to the same grouping.

Among heat-reversible, elastic gels are to be included such systems as:

Gelatin in water,
Agar-agar in water,
Soap in water, and organic solvents,
Dibenzoyl-l-cystine in water (Gortner and Hoffman, 1921, Wolf and Rideal, 1922),
Camphorylphenylthiosemicarbazide in toluene (Hatschek, 1912),
Azomethine in organic solvents (Hardy, 1912),
Cellulose acetate in benzoyl alcohol (Mardles, 1923).

Note: Casein dissolved in alkali + $CaCl_2$ or $Ca(NO_3)_2$ forms a gel on warming and a sol on cooling (Ringer, 1890).

Among heat-irreversible, rigid systems are:

Silica in water,
Celloidin in chloroform and alcohol (Hardy, 1912).
Barium sulphate in water,
Many metallic sulphides and oxides (or hydroxides) in water, etc.

The distinguishing characteristic substances which form heat-reversible gels and those which form non-heat-reversible ones seems to lie in the fact that in the former the temperature-solubility curve is a steep one, rising from a very low solubility at low temperatures, whilst in the latter the solubility curve remains uniformly low at all temperatures or may even fall slightly with rising temperature. As gels are *always produced from supersaturated solutions,* this difference in the character of the two groups is reflected in the modes of preparation employed.

PREPARATION

Where the gelator has a steep solubility curve, the gel state may be attained by making a sol at a higher temperature, and then bringing to a lower. With a substance like gelatin that consists of large, slow-moving molecules, the gelation which occurs on slow cooling in air is spontaneous. With a substance like azomethine, rapid cooling is necessary to produce the super-saturation necessary as a precursor of gel formation.

Gelation can also be induced at constant temperature by dissolving the gelator in a good solvent and adding the solution to a poor solvent, *e.g.,* gel of dibenzoyl-cystine can be prepared by dissolving the crystals in alcohol and pouring the solution into water. The principle, *i.e.,* the production of supersaturation in the solvent, is the same as in gelation induced by cooling. The gel of dibenzoyl-cystine is heat reversible. The gel produced by adding chloroform to a solution of celloidin in absolute alcohol or ether is heat irreversible (Hardy, 1912).

In cases where sols cannot be made by simply warming the solid gelator in a solvent, a gel can be formed by preparing the substance *in situ* in the dispersion medium. For example, silica gel is prepared in this way by dialyzing sodium silicate against water. Sodium and hydroxyl ions diffuse away and the colloidal silica sets to a gel in the dialyzer. Von Weimarn has prepared gels of a number of substances such as barium sulphate, basic chromium sulphate, alumina, etc., etc., by mixing two soluble salts under carefully defined conditions, choosing compounds which by double decomposition produce the gelling body, which is in every instance a *substance highly insoluble* in the solvent employed.

Experimental Investigations of Structure

The methods used for preparing gels suggest that these bodies are formed under conditions which might be expected to lead to the precipitation of the gelator from solution either in the amorphous or the crystalline condition. A visible separation into two phases (precipitate and solution) does not occur, but gels do display properties characteristic of both the solid and the liquid state. Is the gel, therefore, a body in which two phases are potentially present although not separate in the sense of Gibbs' phase rule? Does it, in short, possess an ordered structure? And if so, is this of molecular dimensions only or is it sufficiently coarse to form a system in which it is possible to distinguish between two phases;

Direct investigations on gel structure fall under five headings, namely: (1) microscopical investigations; (2) ultra-microscopical investigations; (3) X-ray analyses; (4) mechanical attempts to separate the two phases; and (5) volatilization of the liquid component or its substitution by another liquid. The great bulk of the evidence bearing on the problem is, however, indirect, and is derived from studies of the physical properties of the gel, and the sol near the gel condition. The indirect evidence falls conveniently into three subdivisions, namely: (1) evidence from investigations on swelling, including changes in volume, density and refractive index, and evolution of heat on gelling; (2) evidence from investigations on viscosity; and (3) evidence from investigations on diffusion in gels and conductivity of electrolytes in sols and in gels.

Microscopical Investigations

The most important microscopical studies of gelation are two papers by Hardy (1899, 2 and 1900, 2) on the formation of irreversible and reversible gels respectively. The irreversible system considered was the coagulation of denatured egg albumen. This system lies rather on the border-line of the gel state, if not, indeed, beyond it. Nevertheless, the structure is of interest. The protein particles formed during coagulation are spheres of 0.75-1 μ in diameter, anastomosing of which become arranged in rows so that an open net with regular polygonal meshes is formed. The reversible system considered by Hardy was one consisting of gelatin-water-alcohol. Hardy chose this system because "the refractive index of one phase differs so much from that of the other as to permit of direct microscopical investigation." He writes "when 13.5 grams of dry gelatin are dissolved in 100 c.c. of an equal mixture of equal volumes of absolute alcohol and water, a system is produced which is clear and homogeneous at temperatures above 20°. As the temperature falls below this limit, a clouding occurs which I find to be due to the appearance of fluid droplets which gradually increase in size until they measure 3 μ. On cooling further these fluid droplets become solid and they begin to adhere to one another. In this way a framework is built up composed of spherical masses hanging together in linear rows which anastomose with one another. The framework therefore is an open structure which holds the fluid phase in its interstices. The macroscopical result of the change is the conversion with falling temperature of the fluid into a loose gel."

Hardy found that rate of cooling had a great influence on structure, the more rapid the rate of cooling, the finer the structure, which he explicitly states may become amicroscopic. He also states that when the concentration of gelatin becomes greater than 36 per cent the structure is altered by the liquid phase becoming discontinuous. This solitary observation is the only contribution known to the writer of the influence of the concentration of the gelator on the structure of the gel. The subject has been conspicuously ignored by later workers.

It seems probable, in the light of later work, that Hardy's microscopical studies were made possible not only by the difference in the refractive index of the two phases, but also by the fact that he produced gels with an abnormally coarse structure.

Further microscopical evidence is Bütschli's (1898, 1900) observation of a fine anastomosing framework (honeycomb) in the partially dried gel of silica. The visibility in this case was attributed to the development of gas bubbles on the walls of the gel framework. His interpretation of his results, however, has been adversely criticized both by Zsigmondy (1911) and by Bachmann (1912).

Microscopical studies of gelation have also been made by Bradford (1920), who considers, however, that gels have a granular structure, and compares them to a pile of shot.

It is to be emphasized that a large number of microscopical examinations of gels have been made without revealing any trace of structure. It is an undoubted fact that, in the majority of gels, the structure, if existent, is of too fine a texture to be revealed by the microscope. Nevertheless, the structures seen by Hardy and by Bradford had a real enough existence, and must therefore be taken into consideration in any theory of gelation.

Ultra-microscopical Investigations

The structure in gels is ordinarily too fine to be visible under the microscope. It is also frequently too fine to be revealed by the ultra-microscope. Zsigmondy (1911) examined the gel of silicic acid and found that both the gel and the fully dried gel residue were optically void. The half dried gel showed the presence of sub-microns. An important observation made was that while gels of a greater concentration than 2 per cent were optically clear, gels of a lesser concentration showed heterogeneity. Agar-agar gels similarly showed no structure visible under the ultra-microscope. Bachmann (1912) examined silica gel and gelatin gel with the same results whilst Laing and McBain (1920) and McBain, Darke and Salmon (1921) found that soap gels were almost free from structure visible under the ultra-microscope except in such cases when the formation of crystals or fibrils had occurred, when the system could no longer be regarded as a gel.

Other workers, however, have found different results. Moeller (1921) states that he always finds strong heterogeneity in gelatin gels. Gortner and Hoffman (1921) state that the gel of dibenzoyl-l-cystine in water has a fine fibrillar structure which is shown by the ultra-microscope. Only patches of the gel show this structure, the remainder being optically void. They suggest that this is due to the fact that the dimensions of the fibrils were close to the working limits of their apparatus. Barrett (1920) states that in the clotting of serum it is possible to demonstrate the formation of long intersecting fibrils by means of the ultra-microscope.

X-Ray Analyses

If gelation is a process of crystallization, then evidence of crystal structure in gels might be expected to be revealed by Bragg's method of X-ray analysis. Only a few gels have so far been examined by this method. Scherrer (1918) found evidence of crystal structure in the gels of silicic and stannic acid, but none in the gel of gelatin.

Katz and Gerngross (1925), however, have found one diffuse and well-defined interference band in the gel of iso-electric gelatin. In gels dried under tension the interference figures become more definite. It seems possible, therefore, that gels contain matter in the semi-crystalline or smectic state.*

Mechanical Separation of the Phases

It is generally impossible to separate a gel into two phases by mechanical means. Hardy (1900, 2) states that it is possible to separate the two phases of an agar-agar gel by gentle friction and squeezing. He gives the following analytical figures:

	Agar in 100 Grms. of the Gel.	Expressed Fluid		Solid Solution	
		Volume	Agar	Volume	Agar
$T = 18°$	1.1 grms.	440 c.c.	0.10%	140 c.c.	4.7%
	3.3 grms.	230 c.c.	0.14%	350 c.c.	5.6%

"Thus an increase in the concentration of agar in the mixture produces an increase in the concentration of the agar in both phases." With strong direct pressure he found it impossible to separate two phases from the gel—"very great force was necessary to express a fluid which was found to be almost pure water."

Gortner and Hoffman (1921) separated the two phases of di-benzoyl-l-cystine by filtration. They found that a limpid liquid filters off and skin of dibenzoyl-cystine remains behind. Wolff and Rideal (1922) say that pure water runs through the filter paper, leaving behind a "crystalline skin" of solid dibenzoyl-cystine. Jordan Lloyd (1920) finds that gelatin gels which have swollen in a dilute acid or alkaline solution, contract on removal to an atmosphere of saturated vapor, and squeeze out a fluid in droplets at numerous *loci* on the surface. This fluid was found always to have a reaction nearer to the iso-electric point of gelatin than that in which the gel had swollen, and to contain gelatin in solution. It was taken by the writer to be the liquid phase of the gel expelled through a disturbance of the osmotic forces due to a readjustment of the membrane equilibria.

Drying, Imbibition and Displacement of One Fluid by Another

If gels are two-phase structures in which the interstices of a solid mesh are penetrated by a liquid, by driving off the liquid, evidence should be obtained as to the nature of the solid framework. The classical experiments of van Bemmelen (1897, 1898, 1902) on the drying of silica gels are the first important contribution to this subject. Van Bemmelen placed the gels over sulphuric acid of varying concentrations until equilibrium was reached. After a certain loss of water had occurred, the gels lost their transparency and became white and opaque. With further drying, transparency returned. On restoring water to the system, a reverse series of changes occurred.

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* See paper by G. Friedel, this volume, p. 102. J. A.

Van Bemmelen accounted for these optical changes by supposing that the gel had a solid framework which was penetrated in every direction by fine capillaries containing liquid. The appearance of opacity at half-drying was attributed to the fact that the liquid phase had been drawn out of the capillaries, but that the rigid solid phase did not collapse, and so a gas phase replaced the liquid in the capillaries. The return of transparency on further drying was attributed to the loss of water from the solid framework with contraction of the walls and closing of the capillaries. The cycle of changes was found to be reversible on restoring water to the system.

Anderson (1914) also studied the loss of water from silica gels on drying. He also supported the theory of a porous structure and estimated the size of the pores in a silica-water gel as from 2.75 to 5.49 μμ. He further allowed his dried silica gels to imbibe not only water but also alcohol and benzene. In the two latter cases he estimates the size of the pores in the fully imbibed gel as 2.42 to 5.15 μμ and 2.70 to 5.98 μμ respectively, *i.e.*, the pores are the same regardless of whether the dispersion medium is water, alcohol or benzene. This fact is strong evidence of a permanent solid structure in the gel, the different fluids having been drawn into the gel by capillary action. Thomas Graham also (1862, 4, 5) made alcogels, sulphogels, etc., from hydrogels of silicic acid in this way.

Gels of gelatin and water behave on drying and during imbibition in a way which is in strong contrast to the silica gels. The gel collapses as a whole during drying, there is no evidence of pores developing, nor is there any stage when clouding of the gel occurs. The dried gels do not re-imbibe any fluid, regardless of its nature as occurred in the case of silica gels, but only water or watery solutions. Nevertheless, the history of the gel has a strong influence on its behavior.

Some recent work by Gortner and Hoffman (1922) shows that both the rate and amount of imbibition of water by dry gelatin grains of equal surface depend on the concentration of the gel from which the grains were prepared, grains dried from a weaker gel taking up more water than those from a more concentrated gel. They consider that these experiments prove that on gelation a permanent structure is formed. Brotmann's (1921) experiments on imbibition are further evidence in support of this view.

Sheppard and Elliot (1922) do not consider that the experimental results of drying gelatin gels justify the assumption of a two-phase structure. They point out that the form assumed by a drying gel with uneven contraction along its three axes, depends on the geometrical form of the gel. They consider that during drying "case-hardening" occurs, and that the restoration of the original form is due to the "original skin-extension." Their arguments, which are valid for the cases with which they deal, do not, however, account for the results obtained by Gortner and Hoffman where different degrees of imbibition were obtained with dry gelatin grains of the same size and geometrical form.

Swelling, Contraction, Density, Heat, Refractive Index

The absorption of water by dried gels is influenced not only by the previous history of the gel itself, but also by other solutes present in the solvent.

It has recently been pointed out in a paper by Huttig (1924), who assumes a crystal lattice in the colloidal state, that water in combination with colloids may fall into four classes.

(a) Water occupying fixed positions in the lattice.
(b) Water free to move in the lattice but in equilibrium with (a).
(c) Water lying freely in the lattice. This is in capillaries of molecular size and subject to osmotic laws.
(d) Water lying in colloidal capillaries, subject to osmotic laws.

While the water taken up by a dried gelatin gel during imbibition in distilled water probably belongs mainly to classes (a) and (b), electrolytes in solution can affect the amount of water absorbed under classes (c) and (d).

The swelling of dried gelatin has been investigated by many workers. This protein swells in water, but to an even greater extent in weakly acid or alkaline solutions.

Procter (1914) investigated the swelling in hydrochloric acid. As a result of his experiments he concluded that if due allowance was made for the Donnan equilibrium at the interface between the jelly and the surrounding fluid then the whole behavior of the systems was in conformity with the laws of mass action as applied to a reaction consisting of the formation of ionizable salts between gelatin acting as a weak base and hydrochloric acid. In the swollen gel the distending forces were osmotic, and due to the excess of free-chlorine ions in the gel as compared with the external solution. The "membrane" between the two phases rose from the cohesive forces of the gel and the non-diffusibility of the gelatin ion. A molecular network in the gel was conceded, but Procter considered gel structure to be of molecular dimensions and gels to be solid solutions.

Procter's work was extended later by Procter and Wilson (1916) and Procter and Burton (1916), but his original views were not altered. The present writer (1920), later repeating and extending the work started by Procter, came to a different conclusion as to the theory of gel structures which best covered the phenomenon of swelling. Working in both acid and alkaline systems, and studying in particular the behavior of the swollen gels on being transferred from a liquid medium to an atmosphere of saturated water vapor, the following theory seemed best to cover the facts: that the gelatin in gels is in two forms, the un-ionized, so-called iso-electric gelatin and the ionized salt form, *i.e.*, gelatin hydrochlorides of various degrees of saturation or sodium gelatinates as the case might be; that the un-ionized iso-electric gelatin formed a solid framework through the gel and was the seat of the elastic forces; that gelatin in the form of ionized salts was present in solution in the liquid phase of the gel and was the origin of the distending (osmotic) forces; and further that unless both forms of gel were present, the gel state would be an unstable one, *i.e.*, that for a gelatin-water gel the existence of a third substance, such as a gelatin salt, was necessary.* This prediction was confirmed later by the writer (1920) and by Field (1921), Smith (1921) for one per cent gels, though the latter found that higher concentration gels were more stable. It is interesting that Jordis (1902) also found a third component to be necessary for the formation of silica gel.

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* Since gelatin is not a definite chemical entity, it is questionable to speak of "gelatin chloride," etc. The phenomena may be consequent on the co-existence of larger and of smaller aggregations, the larger ones devoid of kinetic motion, the smaller ones nearer to solution. See "Glue and Gelatin," by J. Alexander, A. C. S. Monograph, 1923. J. A.

The osmotic nature of certain types of swelling found with gelatin has not been demonstrated directly for other gels, but Dokan's (1924) recent work on the swelling of agar-agar suggests that the state of aggregation of the gel colloids or coherence of the gel framework is influenced by electrolytes in solution which thus affect the behavior of the gel. Katz and Mark (1924-1925) have shown that with inulin and cellulose under certain conditions swelling is accompanied by an enlargement of the crystal lattice, but too much stress cannot be laid on this evidence as they were not dealing with gels in the strict meaning of the term.

Katz (1918) studied the swelling of gelatin gels especially from the point of view of the changes of the total volume of gel and imbibed fluid, and of the evolution or absorption of heat. As is well known, during swelling there is a loss of total volume and an evolution of heat. Katz states that the behavior of a gelatin gel while swelling is exactly parallel to that of a strong solution on dilution, and compares it especially with the two systems sulphuric acid and water, glycerin and water, and concludes therefore that a gel is a solid solution.

Mardles (1923), dealing with the organosols and gels of cellulose esters and resins, finds that the volume contractions are in general smaller than those in aqueous systems. Following density and refractive index changes, he also states that although there are no breaks in the curves over the sol-gel transformation zone, there is a definite change in direction that indicates a change in molecular aggregation or pattern as the passage from sol to gel takes place. He also considers that Walpole's (1913) data on the refractive-index-temperature curve in gelatin indicate a change of direction near the setting point. Walpole himself regards the curve as linear, and Davis and Oakes (1922) and Taffel (1922) consider the density concentration curve of gelatin gels over the setting point is linear.

Laing and McBain (1920) find the refractive index of a soap sol is unaltered on setting.

Viscosity

The viscosity of a heat-reversible gel rises steadily with falling temperature until the sol passes without any abrupt transition into a gel. It has, therefore, been held that a gel is only a limiting case of a viscous liquid and is free from any ordered and rigid structure.

Two recent papers by Bogue (1922, 1) and Mardles (1923, 2) dealing with aqueous and non-aqueous systems respectively, both suggest that the slip occurring in gelling systems near gelation is more characteristic of a plastic solid than of a viscous liquid, *i.e.*, there is definite though small resistance to shear. Bogue was examining gelatin-water, and Mardles cellulose acetate in benzyl alcohol. These observations both count against the idea that gelation is due merely to increased viscosity. It is interesting also in this connection that the p_H range of increased viscosity of gelatin-water sols (Loeb, 1922) corresponds to the range of diminished capacity for gelation (Jordan Lloyd, 1922). Among other workers may be mentioned Garrett (1903), van Schroder (1903), Levites (1908), Gokum (1908), Schorr (1911) and Hess (1922). All these have found a time factor in viscosity measurements which can be accounted for by assuming that during the time occupied in reaching constant values for the viscosity, a definite orientation of molecules or particles is taking place in the system.

DIFFUSION AND CONDUCTIVITY

The evidence on the diffusibility of electrolytes through gels has always had an important bearing on the question of structure. Graham (1850, 1851, 1862) found that crystalloids in general can diffuse through a gel at a rate which differs by very little from their rate of diffusion in water. These results were confirmed by de Vries (1884), Voigtlander (1889) and Dumanski (1907). The recent work of Stiles and Adair (1921) and Stiles (1923) on the penetration of electrolytes into gels has also led these two investigators to conclude that chlorides and sulphates diffuse through gels in the same manner in which they diffuse through water, and they again emphasize the comparatively slight influence which concentration of the gel has on the diffusion rate compared with its influence on viscosity. They find that in gels (gelatin and agar-agar) increased concentration of gelator up to 2 per cent tends to decrease the rate of diffusion of the electrolytes. Further increase leads to further but very slow decrease in the rate of diffusion. They consider that these facts can be brought into harmony with the usual diffusion equation, namely

$$\text{Diffusion} = f \frac{1}{\text{viscosity}}$$

by supposing the first addition of gel substance to increase the quantity in solution, increasing viscosity and decreasing diffusion in the normal way, but that later additions (2 per cent up to 16 per cent) have only the effect of adding to a solid structure. It seems a pity that a few observations were not made at 36 per cent on the gelatin gel where, according to Hardy (1900), the liquid phase becomes discontinuous, and therefore diffusion should cease.

The experimental work of other writers on the hindrance by gels to the diffusion of colloidal dyes (Herzog and Polotzky, 1914) is in harmony with the theory that diffusion has to take place through the capillaries of a sponge-like structure, since, where the capillary diameter and the diffusing molecule become of the same order of magnitude, this interference might be expected.

The work on diffusion illustrates most conspicuously the great difference between a gel and the extreme case of a viscous fluid, a glass.

Some interesting work is reported by Callow (1925) on the velocity of ice crystallization through gelatin gels supercooled to —3°. In such gels seeded with an ice crystal, the ice face advances slowly through the gel along definite tracks, at a rate depending on the concentration of the gelatin and of any electrolytes present. If such a frozen gel is thawed, recooled, and again seeded with the crystal, separation of ice now takes place at an enormous rate, apparently along the tracks previously made. These facts suggest that the first separation of ice had irreversibly ruptured some rigid structure in the gel.

Very closely allied to the evidence on diffusion is that on conductivity in and by gels. Here again in both sols and gels the interference with the migrating ion is of a very much lower order of magnitude than might have been anticipated from viscosity measurements. Graham (*loc. cit.*) considered that the presence of the gel substance does not affect conductivity and Arrhenius (1887) states that in a system consisting of gelatin, water and salt, the conductivity is the same in both sol and gel. Laing and McBain (*loc. cit.*) find in a system soap-water, conductivity is the same in both sol and gel state at the same concentration of soap and at the same temperature. Martin Fischer, however (1924), finds that the electrical resistance of soap solutions shows a very marked increase at and below the gelling temperature. In both these series of experiments the conducting ion and the gel forming material both come from the same source. Hatschek and Humphry (1924) have measured the conductivity of copper sulphate in the presence of agar at 50°. At this temperature both the gel and sol condition of agar solutions can be maintained indefinitely. In this system the colloid and the conducting ion have an independent origin, and it was found for both direct and alternating current that the conductivity was about 2 per cent higher in the gel than in the sol at the same concentration and temperature. The results are interpreted as showing that the migrating ions travel only in the liquid phase of the gel, where their speed of movement varies inversely as the viscosity. In a gel the viscosity of the liquid phase is less than in the sol at the same concentration and temperature owing to separation of part of the colloid as a solid phase.

GELATION AND CRYSTALLIZATION

Gels have mechanical properties of solids and the weight of evidence supports the theory that they have a rigid phase which possesses the characters of a solid. The problem remains as to whether this solid phase is amorphous or crystalline. The results of X-ray analysis are only definite with certain gels such as the hydrogel of silica and of stannic acid; with the hydrogel of gelatin, the question seems to be left open, though the recent work of Katz and Gerngross (*loc. cit.*) is suggestive of molecular orientation. Levites (1908) compared gelatin to crystallization and Von Weimarn (1908) who defines as "crystalline" any solid unit (from a single molecule upwards) having asymmetrical fields of force around it, considers that all precipitation is crystalline in nature, and he regards gelation as a limiting case of precipitation.

After an extensive investigation on the form of precipitates, he summed up his experimental results in the form of the following equation:

$$N = K \frac{P}{L}$$

where L is the solubility
P is the degree of super-saturation
K is a factor involving viscosity
and N is the number of crystallization centers.

The factor P is naturally influenced by the diffusion constants, *i.e.*, by molecular mass, and both P and K are functions of the temperature.

Where K and P are small, and L is (relatively) large, the value for N will be small and the resulting precipitate will be in the form of a (comparatively) small number of large crystals. Where K and P are large, and L is small, N will be at a maximum and the precipitate will be in the form of an enormously large number of infinitely small crystals. Under this condition the whole system sets to a gel which von Weimarn describes as "ein krystallinisches Schwamm" (a crystalline sponge). Von Weimarn's equation summarizes the empirical facts that high molecular weight and low solubility are frequently the properties of gelling substances and that conditions which lead to super-saturation, such as rapid cooling or very slow mixing of solutions, also favor gelation.

During the last few years the classical work of the Braggs has made clear the distinction between amorphous solids and crystals. An amorphous solid is really only the limiting case of a liquid. In the majority of liquids the units have considerable powers of changing their place in the system. Much evidence is slowly accumulating that in liquids the molecules may be associated into groups of twos, threes, or perhaps even higher numbers. Although the molecules in these groups must be arranged in a definite order in their relations to each other (Bragg considers that the groups must be capable of being embodied in the elementary crystal units (1923)), the liquid as a whole is an asymmetrical agglomeration of units. The freedom of the units to move over each other is measured by the viscosity, and in cases where the viscosity is infinitely great, the power of translational movement of the units is lost and the system becomes an amorphous solid or glass. It is still a system without symmetry. It is now known that in crystals the units are arranged in a pattern which has a definite symmetry in three-dimensional space. In crystals such as sodium chloride the units are the individual atoms, but in crystals of organic substances the molecular pattern is preserved and the molecules are oriented into a definite three-dimensional pattern. The essence of the true solid state, the crystal, is structural order. The attainment of this order is accompanied by the evolution of heat—the latent heat of crystallization. It might therefore be thought possible to obtain evidence as to the nature of the solid phase in gels by a study of the heat relations of gelation, but very little experimental work has been recorded. Wiedemann and Lüdeking (1885) point out that although dry gelatin absorbing water liberates heat, yet on solution heat is absorbed. As gelatin becomes more soluble with rising temperature, therefore, it behaves like the majority of crystalloids. Mardles also (1923) points out that the maximum gelation temperature-concentration curve of cellulose acetate in benzoyl alcohol resembles the temperature-saturation concentration curve of crystalloids. Hardy (1912) finds that with azomethine gels a certain quantity of heat has to be withdrawn from the system in order to bring about gelation, but that a further quantity has to be withdrawn before the true crystals separate. He points out the similarities between gelation and crystallization, namely that a solution may be super-cooled with respect to gelation and that such supercooled solutions may be caused to gel by (1) slight warming, (2) rapid shaking, (3) sowing with already formed gel. The presence of nuclei in a solution also favors gelation, and in the case of azomethine gels even seems to be essential. Nevertheless Hardy concludes: "The process has many points of resemblance to crystallization but the masses (of azomethine gel) are not crystals unless the sphere be admitted as a crystalline form." Again: "These masses (of azomethine gel) have all the appearance of crystals. They are not crystals, however. They are singly refractive. . . . The true crystals of azomethine are doubly refractive." "The gel never changes directly into crystals. The true gel is completely stable with respect to crystals, but the component large masses melt at their surfaces only and the fluid so formed deposits crystals."

It is perhaps valuable to recall at this stage the anomalous form in which crystals separate from solutions in which colloidal material is present. Reinders (1911) gives as an example the crystallization of silver chloride in the presence of methylene blue. The crystals are elongated and branched. The writer has found that glucosazone separating in the presence of dextrin may appear as globules and fail entirely to take on the well-known crystalline form. How far these anomalous crystals have an orthodox space lattice is unknown.*

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* See paper by J. Alexander, this volume, p. 11. J. A.

The Theories of Gel Structure

The theories that have been put forward to account for gel structure can be classified under four headings.

The Solid Solution Theory of gels is supported by Procter (1914), Procter and Wilson (1916), Hayes (1914), Katz (1918), Sheppard and Elliot (1922) and Laing and McBain (1920). Laing and McBain consider that in both sol and gel of soap and water systems there are "ionic micellæ" which may become visible under the ultra-microscope. There is therefore in their theory a possibility of a second phase, but it has no connection with the sol-gel transformation. Martin Fischer (1924) has suggested that gelation of soap solutions is due to the inversion of a "soap-in-water" to a "water-in-soap" solution.

The Liquid-Liquid Theory of gel structure was proposed by Ostwald (1909). It has already been stated that viscosity experiments had suggested that the gel was the limiting case of a viscous liquid. The viscosity of a solution is a function of the volume occupied by the solute and where the system consists of two immiscible fluids, the viscosity is a function of the concentration of the dispersed phase (Hatschek, 1912). A highly viscous system such as a gel might, therefore, conceivably be formed by the separation of two liquid phases. Hatschek (1916, 1917), however, has shown that the mechanical properties of such a system do not correspond with those of true gels. Hardy finds that an emulsion of ether and water can be made to simulate a gel by the addition of a trace of iodine which forms a solid film at the interface of the two fluids (personal communication).*

The Solid-Liquid Theory, in various forms, is the one which has to-day the adherence of the majority of workers on colloids.

The Micellar Theory of gel structure postulates a discontinuous granular solid phase dispersed through a liquid phase. This theory carries with it the halo of tradition. Frankenheim (1835) and van Nägeli (1858) both considered the solid part of a gel to be crystalline. Van Nägeli considered that gelation was due to the separation of numerous crystalline micellæ, each of which carried round itself concentric shells of the dispersion medium. The solidification was thus due to the adsorption of the major part of the fluid on the micellæ. The micellar theory in its essential details is supported by Zsigmondy (1911), Bachmann (1912), Arisz (1915, from observations on Tyndall cone effects), and Bradford (1918, 1920, 1923).

The alternative form of the solid liquid theory can be called the *Fibrillar Theory.* It differs in mechanical pattern from the micellar theory in that the solid phase is assumed to be continuous. It appears to have been first suggested by van Bemmelen (1898), but was also put forward by Butschli in the same year. In Bütschli's "honeycomb" theory the fluid phase was held to be discontinuous. Most workers, however, regard both solid and liquid phases as continuous. Almost since the year of its origin, the solid-liquid two-phase theory of gels has given rise to discussion as to whether the solid phase is crystalline or is a solid solution. The problem is not without its difficulties. Even a separation and analysis of the two phases, if it could be achieved, would not be conclusive, since wherever there is an aggregation of molecules to form a rigid type, there is in a sense a new phase, and at the interface between solid and liquid, the liquid will be adsorbed and oriented (see Parks,

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* Holmes has recently reported on emulsions made with iodine. See 2nd Colloid Symposium Monograph, 1925.

1902, 1903; Hardy and Doubleday, 1923). There seems to be very little doubt nowadays that in rigid gels of the silicic acid type, the solid phase is crystalline. In the elastic or heat-reversible gels the matter is more doubtful. It seems possible that in all gels the tendency is toward a crystalline structure, but that in some at least crystal formation is prevented, and the solid phase remains nearer in kind to the solid solution. The pattern of a gel as a three-dimensional solid framework or felt-work of fibrils which become joined at their points of intersection and so form a framework in the spaces of which fluid lies, was originally put forward by van Bemmelen, and has in its main plan received the support of Hardy (1899, 2, 1900), Freundlich (1922), Brailsford Robertson (1918), von Weimarn (1907, 1908), Hatschek (1912), Barrett (1921), Gortner and Hoffman (1921), Wolf and Rideal (1922), Bogue (1922), and the writer (1920), etc. The mechanism by which the framework comes into being is a matter on which different workers have different views. Hardy and von Weimarn regard it as due to the separation of a new phase, the latter as specifically due to crystallization, Brailsford Robertson to the coarsening of a pre-existing structure, Bogue to the elongation and hydration of catenary threads of hydrated molecules. Wolf and Rideal give an ingenious model of fibril formation, wherein the residual fields of the electrically unsaturated groups—S — S—(positive), carboxyl (negative) and the benzoyl-amino group (negative) are shown as linked resulting "in the formation of molecular aggregates arranged in echelon permitting the growth of needle-like or fibrous crystals."

If gel formation depends on the number of centers of crystallization, *i.e.*, on the number of centers where the molecules of a dissolved substance are coming together in an ordered pattern, it does not seem impossible that where the number of these is very great, the molecules may form chains rather than solid blocks. At present the study of molecular pattern is in its infancy and more experimental data need to be accumulated. The relation of the gel substance to the solvent also needs further study. In the case of gelatin and water, there is undoubtedly association between the two (Jordan Lloyd, Bradford, Bogue, etc.). Bogue has been so impressed by this fact that he has perhaps rather over-emphasized its importance in the gelling process. Since there is no association between water and dibenzoyl-cystine (Wolf and Rideal), nor between camphoryl phenyl thiosemicarbazide and alcohol (Hatschek), and yet since both these systems form gels, the association between solvent and gelator is obviously not a *sine qua non* for gel formation. Moreover, even in the case of gelatin and water, the following statements, all founded on experimental evidence, have to be brought into harmony:

(1) That the viscosity of a sol is due to the hydration of the particles. (Hatschek).
(2) That the ionized particles in a protein solution are more heavily hydrated than the non-ionized (Hardy, Hatschek, Loeb).
(3) That the gel framework is formed from un-ionized gelatin (Jordan Lloyd).
(4) That viscosity varies with reaction (p_H) (Loeb).
(5) That over the same p_H range where viscosity is increased, the tendency of the sol to gelate is decreased (Jordan Lloyd).

It is obvious, therefore, that mere hydration of threads is not a cause of gel formation, although it accompanies it in the case of the gelatin-water gel. *There is no need to assume that all gels have the same molecular archi-*

tecture.—There is little doubt, however, that they all possess a solid phase, and have therefore definite molecular orientation on both sides of the interface. Some important work in the shape of gas bubbles in gels has a bearing on this point. As is well known, gas bubbles produced in a fluid (however viscous) are always spherical, but gas bubbles produced in gels are lenticular. This shows that the strains in the gel have a certain orientation. But the orientation of the lenticular bubbles is entirely fortuitous (Hatschek, 1914), *i.e.,* the gel differs from the crystal in having no cleavage planes. There is no doubt, however, that crystallization and gelation are very similar processes. On the theory put forward above, crystal formation and fibril formation would also be of a similar nature, and the recent interesting observation of Bailey (1923) that in saturated solutions of salicylic acid the solutions may deposit crystals in *fibrils,* opens up a new field of experimental study.

Conclusions

1. A gel is a system which possesses mechanical rigidity yet allows diffusion to proceed throughout its mass at a rate similar to that in liquids. It must therefore contain molecules which only vibrate about a mean position, and which constitute a solid phase, and molecules which migrate throughout the system and constitute a liquid one.
2. Gels consist of two components, a liquid solvent, and a solid solute. The determining property of the solute is that at the temperature range of the gel state, it is only very slightly soluble in the solvent.
3. Gels are only formed from super-saturated solutions.
4. Two-component gels are unstable systems and break up sooner or later into solvent and crystalline solvee.
5. The addition of a third component which may be the gelator in salt form frequently stabilizes the gel condition.
6. The mechanical properties of a gel may be based on two models:
   - a. Where there are two continuous phases, one liquid and the other a solid solution. With increasing concentration of gelator in this model the liquid solution phase will finally become discontinuous and the system will approximate to a glass. Agar-agar and commercial gelatin gels probably belong here.
   - b. Where there are two continuous phases, one liquid and the other solid, but with the molecules in the solid phase showing *structural order, i.e.,* showing the property characteristic of crystals. Dibenzoyl cystine and most of the true two-component gels probably belong here.
7. An emulsion of two liquids can be made to simulate a gel if a third component is introduced which forms a continuous solid film at the interface.
8. Gelation is a process closely parallel to crystallization and accompanied in most cases by evolution of heat. When crystallization occurs from a gel, however, there is a further evolution of heat. Gelation therefore is a partial transformation of the gelator from the liquid to the solid state.

In conclusion it is suggested that the great need at the moment in the study of gels is a re-investigation of gel properties in systems uncomplicated by ionic reactions between gelator and solvent such as occur in nearly all the hydrogels of gelatin. A beginning has been made in this direction in the recent work of Mardles, but a full investigation of the physical properties of a system where the gelator is a substance of known molecular structure, which can readily be obtained chemically pure in crystalline form, and where the solvent is an inert organic fluid of (as near as possible) the non-associating type, would undoubtedly throw fresh light on the mechanics of the gel state. Most important of all would be evidence on the dimensions of the gel framework, and on its nature (crystalline or amorphous); on the orientation of molecules on either side of the interface between solid and liquid; and on the nature and strength of the forces acting at and across this interface.

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Diffusion in Jellies

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Diffusion in jellies is free from those convection disturbances, which are hardly to be avoided in liquids. When, coincident with the diffusion, a chemical reaction forms insoluble products, these remain at their place of origin if the diffusion establishes a state of pronounced supersaturation. The phenomena of supersaturation are more distinct as there is no convection and the distribution of nuclei is controlled—in any event there is to be considered the possibility of a chemical or colloid-chemical reaction between the substance diffusing in and the substance forming the jelly.

Similar is the behavior of porous bodies, whose pores are filled with liquid to such an extent that there is no chance of capillarity causing motion of the intruding liquid. Therefore observations made on jellies are of great importance for the explanation of the phenomena of diffusion in mineralogy and geology.

As with liquids, here too we must differentiate between the quantity of the diffusible substance, which intrudes per unit of time and of volume, and the distance covered per unit time. This means that there are two different kinds of "speed of diffusion." When $AgNO_3$ intrudes into a jelly of gelatin containing NaCl, its path is shorter than in a jelly free from NaCl, because the concentration of $AgNO_3$ is constantly diminished by the formation of AgCl. At the same time the rate of concentration becomes more rapid. In consequence of this the quantity of substance intruding into the jelly is increased according to the law of Fick.

Between jellies and porous bodies filled with liquid, several investigators have seen only a quantitative difference. The pores in jellies are said to be merely very much smaller. The ultrafiltration of Bechhold seems to support this assumption. According to this view, diffusion is said to take place only in the liquid, which fills the pores. The solid part diminishes the quantity of water and therefore must diminish the quantity and the path of the substance diffusing in. Besides we must remember that in this view of the nature of jellies, a great part of the water can be in a special condition, because it is condensed by adsorption at the capillary walls. The differences from a diffusion in pure water may become still greater by assuming, *e.g.*, as did Wo. Pauli, that certain jellies are not only ultraporous but also heterogeneous. Diffusion is slightly obstructed by the jelly-forming substance.

In recent times one has often looked upon the motion and the dispersion of colloidal particles in water as being of the same nature as that of sugar molecules in water (a non-electrolyte is chosen to avoid the complications involved by ionization). But the Brownian motion is caused by the impact of the molecules of the solvent, whereas in the case of the sugar molecules there exists in addition another tension toward dispersion, which is independent therefrom. Only the latter should be called diffusion. Bayliss has shown that the Brownian motion ceases as soon as a gelatin solution stiffens to a jelly. But this is not the only reason why a spontaneous movement of colloidal particles is usually impossible in a jelly.* Colloidal particles are mostly thicker than the hypothetical capillary tubes of the jellies. Molecularly dispersed solutions of substances with a very great molecular weight (*e.g.*, hæmoglobin) which at the same time belong to the sphere of colloids, may for the same reason be prevented from intruding into jellies, though they may really diffuse in aqueous solutions. The mechanism of the ability of a freshly prepared SiO_2 sol to dialyse still remains unexplained. Perhaps in this case the osmotic pressure of molecularly dispersed substances present in the liquid, causes a sort of ultrafiltration.

Dialysis is practically the same thing as diffusion in jellies, only it permits us to recognize more distinctly the processes going on inside of the membrane. As the water on one side of the membrane is continuously renewed, the thinness of the membrane produces an extraordinarily rapid rate of concentration.

A characteristic experiment to show a reaction between the diffusing and the jelly-forming substance, is one with $FeCl_3$ and gelatin-jelly. Either $Fe(OH)_3$ is adsorbed by the gelatin, or a chemical compound is formed with the gelatin. This brownish colored gelatin is strongly tanned. HCl migrates in advance and causes the gelatin to swell.

In such reactions with the jelly-forming substance or with substances which are distributed in the jelly, the diffusion is in most cases sharply limited in contrast to the very quiet and gradual diffusion, when there is no reaction. But in the case of a reaction with a (soluble) constituent of the jelly, there may also be no sharp limitation, when the product of reaction, before assuming the solid state, is still in supersaturated solution.

HCl intruding into a gelatin-jelly to which an indicator has been added, shows not only a very sharp limit, *e.g.*, from red to blue in presence of litmus, or at a somewhat different place from white to red in presence of slightly alkaline phenolphthalein, but also independent therefrom a limit in which the isoelectric point is reached, and which is distinguished by characteristic refraction of light. The rate of concentration existing in such a preparation, renders it comprehensible that in a local formation of acid in the jellies of an organism, there may be successively reached those p_H's in the surroundings, which form optima for the action of enzymes, etc.

When in a cylindrically formed jelly NaCl intrudes from one side and $AgNO_3$ from the other side, both diffusion streams meet nearly in the middle of the cylinder, with formation of AgCl. N. Pringsheim has stated that such a precipitation membrane always develops to that side where the (molecularly) less concentrated solution is present. When NaCl and $AgNO_3$ are present in equivalent concentrations, the membrane expands only slightly but grows extraordinarily dense. In this case intersusception instead of apposition takes place. These membranes can assume a very high degree of impermeability. In the former case the membranes are partially permeable, so that by subsequently raising the concentration of the weaker solution the precipitation membrane grows in the opposite direction. This seeming semipermeability is therefore dynamic in nature. The formation of a precipitate is not necessary for it. Also in organisms many membrane-like actions may be imitated by such conditions.

Some seeming exceptions to the rule of Pringsheim can be explained by the diffusion of the supersaturated solution first formed by the product of reaction. In this way the precipitate can expand between the circles of diffusion of $K_2Cr_2O_7$ and $AgNO_3$ in both directions, producing sometimes peculiar structures, which resemble garlands or wreaths.

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* In ultrafiltration they are impelled by the external pressure which has a relation to the Brownian motion and not to the diffusion.

On immersing a layer of gelatin-jelly containing some NaCl of medium concentration in solutions of $AgNO_3$ of different concentrations, formation of AgCl inside the jelly takes place only when the $AgNO_3$ solution is of a definite concentration. In other cases NaCl diffuses out of the jelly into the surrounding liquid, and the jelly remains free from AgCl. Between this exogenous and endogenous formation, a superficial membrane of AgCl develops, which can become very dense. On putting jelly layers containing NaCl solutions of different concentrations in an $AgNO_3$ solution of medium concentration, similar results are obtained.

The salt present in the jelly acts to the salt in the aqueous solution as if it were less concentrated. On adding gum arabic or another hydrophilic colloid to the outer liquid, the solution behaves, on diffusing in, as if it were less concentrated. These phenomena suggest the addition of a hydrophilic colloid, which is able to replace to a certain extent the colloids of the blood-serum, to physiological salt—or the Ringer's solution.

On trying to test for a phosphate (such as Na_3PO_4) within a jelly, with molybdate reagent, in all proportions of concentration a precipitate is formed exclusively in the outer liquid. This is verified by the fact that molybdic acid, according to L. Wöhler, is not dissolved to molecular dispersion but only to colloid dispersion. Hence it is unable to diffuse into the jelly. When the jelly contains $Ca_3(PO_4)_2$, the formation of the precipitate goes on in the same way in the outer liquid, because the Ca salt is dissolved by the HNO_3 diffusing in. MacCollum, among others, has tried to test with this reagent for phosphates *in situ* in histological preparations. These and other experiments of like kind must prove a failure.

The reason is that soluble salts distributed in a jelly always diffuse in the direction of the precipitate-producing substance which has diffused in, because precipitation means removal of ions, which tend to distribute themselves equally in a given space. Hence a decrease of concentration is formed round a drop of $AgNO_3$ which has been put on a jelly layer containing NaCl. If two drops of $AgNO_3$ are put on some distance from each other, deformations of the AgCl rings are obtained when the two coronas touch. Between the two drops there can be finally no replacement of NaCl from greater distance. There the $AgNO_3$ finds less resistance and can proceed further than in other directions. The AgCl masses seem to attract each other. When they meet lemniscate-like curves are formed such as are found in geology in the lime concretions of Imatra-stone. Perhaps also the growing towards each other of the lime precipitations of two neighboring centers of ossification, can be thus explained.

Coronas of reduced concentration are also formed when the substance is removed at particular places by other means. When a little bit of charcoal is placed on a jelly containing methylene blue, equally distributed, the dye migrates to the carbon because it is adsorbed there. In this case also the rate of concentration becomes so very rapid that in the neighborhood of the carbon a considerable decolorization takes place. Those places in a living tissue, at which synthesis of albumin occurs, seem to attract amino-acids from the milieu, because these constituents of albumin there disappear from solution. This is an essential factor in assimilation.

A piece of jelly containing NaCl when placed in a stronger solution of $AgNO_3$ is certainly penetrated by the latter. But the inner part remains free from AgCl, because all NaCl there has diffused in direction to the $AgNO_3$. Hence it is impossible to dye a histological preparation uniformly with silver chromate according to the process of Golgi, because the $K_2Cr_2O_7$, with which it was fixed, diffuses in direction to the $AgNO_3$.

For the same reason $AgNO_3$ diffusing in a cylinder of jelly containing NaCl, or alkali diffusing in a jelly containing acid, finally undergoes acceleration; for then these salts find less resistance.

At the very beginning, the diffusion inward occurs much more quickly than after a few hours. Below the drop of $AgNO_3$ placed on a jelly layer containing NaCl, the AgCl can be of such a high degree of dispersity that this zone is nearly transparent. Above it a very strong opacity is formed. There the NaCl had more time to diffuse in direction to the $AgNO_3$ and thus the concentration of the AgCl becomes a little higher. Below the drop the AgCl had no time to form larger aggregates of molecules. In many other reactions the newly formed substances get much less disperse at greater distances from the surface. On reduction of $AuCl_3$ in a jelly of SiO_2, E. Hatschek obtained crystalline flakes of metallic gold of a few mm. in size. This means that many natural minerals do not require so long a time to be formed as is generally assumed, when they are formed by diffusion.

A suspension of AgCl, as used in photographic practice, prepared in a solution of gelatin with slight excess of NaCl, when poured on a glass plate gives a layer of only very slight opacity, the AgCl being still of a very high degree of dispersity. A drop of $AgNO_3$ put on its surface does not increase the opacity, in spite of the additionally formed AgCl. But this occurs to a very marked extent in the neighborhood of a drop of NaCl. In this case AgCl is dissolved intermediately and it is possible that some particles grow at the expense of others. This way of diminishing the dispersity is called "Ostwald ripening." An analytical chemist neglecting this fact might have concluded from the increase of opacity on addition of NaCl that there was an excess of $AgNO_3$ in the jelly.

When an acid acts upon a mixture of powdered $CaCO_3$ and $Ca_3(PO_4)_2$, $CaCO_3$ is dissolved preferentially. The residue therefore contains relatively more $Ca_3(PO_4)_2$. For this reason Levy declared the acid theory of rachitis and osteomalacia to be erroneous, because on analyzing these pathological bones, he found the usual proportion between $CaCO_3$ and $Ca_3(PO_4)_2$, *i.e.,* no relative enrichment of the latter. But when both substances are distributed in a jelly they are *both* dissolved by an inwardly diffusing acid as far as it intrudes. On the other side of this limit the previous proportions remain unchanged. Thus the progress of the reaction is essentially changed, and the objection of Levy against the acid theory of these diseases is without foundation, though it was so acceptable to orthodox chemists, that for many years one hardly dared to advance a theory of these diseases.

When a gelatin jelly containing NaCl dries on a glass plate, a portion of the NaCl diffuses from the borders, drying first to the middle of the plate. From this impoverishment of the borders in soluble halide, Homolka has deduced the formation of a sort of veil at the borders of photographic plates. When, on drying, changes of temperature or irregular currents of air occur, these are marked by stronger and weaker crystalline spheres of salt, if it was present in excess. For some salts a change of exterior conditions is not necessary to produce such segregation. Rather regular segregation can be obtained, *e.g.*, by drying a layer of gelatin jelly containing Na_3PO_4. E. Küster especially has studied these rhythmical crystallizations.* In connection with the theory advanced by Wilhelm Ostwald for the rhythmic precipitation of silver chromate, one can suggest also in this case that the salt, on progressive drying, first reaches a state of supersaturated solution, and that afterwards the metastable limit is reached at one place, where the transition into the solid state occurs without presence of nuclei. Then a portion of the supersaturated solution diffuses from the neighborhood to the nuclei thus formed, where it becomes solidified as well. But of course we must still explain why the entire solution does not migrate to these nuclei. It is possible that this intermittent condition is produced by the drying of the jelly layer in the neighborhood of the nuclei, so that the diffusion becomes too slow, and a second and further metastable limit is reached only at some distance from the first one. Therefore it seems unwise from the observations made on plane preparations to infer immediately an explanation for the flaky decay of sandstone used in buildings with cement containing lime. Though in this case diffusion plays an important part, capillary action is an additional and a very essential factor.

The supersaturation, produced in rhythmic crystallization by loss of water, may also occur when a diffusing salt reacts with a second one equally distributed in the jelly, with formation of a difficultly soluble salt. Wo. Ostwald describes the following experiment: fill a test tube to the height of 15 cm. with a solution of 4 g. gelatin, 0.12 g. $K_2Cr_2O_7$ in 120 g. of warm water. After the jelly forms pour over it a 5 cm. layer of 8.5 g. $AgNO_3$ in a 100 c.c. of water. Or distribute the jelly in a thin layer on a glass plate and put on it a large drop of the $AgNO_3$ solution. When the latter diffuses, many horizontal thin layers of $Ag_2Cr_2O_7$ are formed, which are separated by broader layers free from or containing only very little precipitate (the complications caused by the facile change of $Ag_2Cr_2O_7$ into Ag_2CrO_4 may be overlooked). On the glass plate many concentric rings are formed round the drop. In many other reactions similar rings appear. In a gelatin jelly E. Hatschek produced rings of $Ca_3(PO_4)_2$, $CaCO_3$, and $BaCO_3$, J. Alexander rings of Prussian blue, Morse and Pierce of $BaCrO_4$, $Cu(OH)_2$, and HgBr. Alkaloids, according to Handovsky, are precipitated rhythmically on diffusing in gelatin containing $K + I$. The distances become especially large when on experiment with silver chromate a little citric acid is added to the jelly; or when, according to J. Tillmanns, $MnSO_4$ diffuses into a gelatin jelly containing NH_3. In agar jelly, according to Hatschek, PI_2 and $PbCr_2O_7$ are separated rhythmically; according to R. Fricke, also thallo-iodide. In SiO_2 Hatschek and H. N. Holmes produced striped metallic gold; the latter also produced $CuCrO_4$, Cu_2O, HgI_2, and $HgCl_2$.†

It is a question whether the supersaturation theory of Wilhelm Ostwald, already referred to, is sufficient in itself to explain the phenomena. In spite of the objection made by Hatschek, it seems to be a certainty that supersaturation plays an important part. But there must be still another factor which corresponds to the drying of the corona in rhythmic crystallization. H. Freundlich thought that he could assume the "flocculation" of a primarily formed sol. But against this theory the objection was raised that in a jelly a motion of colloids can hardly be expected. According to S. C. Bradford, the formation of a corona is increased and therefore the rhythmic formations are rendered possible by the fact that $Ag_2Cr_2O_7$ adsorbs $K_2Cr_2O_7$ on itself and thus, so to speak, draws it out of the milieu. But in the sphere where $AgNO_3$ and $K_2Cr_2O_7$ meet each other and react, there is no solid $Ag_2Cr_2O_7$ present at all at the beginning, but only dissolved $Ag_2Cr_2O_7$ in the state of supersaturation. Therefore it is hard to believe that an adsorption of $K_2Cr_2O_7$ on $Ag_2Cr_2O_7$ takes place in that region. In any event some work is still necessary to explain rhythmic formation.*

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* See also paper by du Noüy, this volume. J. A.

† See paper by H. N. Holmes, this volume. J. A.

The bands in agates have been explained as a rhythmic precipitation of an iron compound in the original SiO_2 jelly. The preliminary jelly-like state of the mineral, which is later on so very hard, has been found in nature. Furthermore, the precipitation of $Fe(OH)_3$ in rings in an SiO_2 jelly is easily produced experimentally. But agates often show such sharp corners in their structure that considering the tendency toward rounding in diffusion preparations, one feels inclined to doubt the resemblance in mode of origin. Perhaps the crystallization of the jelly took place at the same time as the formation of the rings in the agate. There is much more resemblance to the artificial preparations in certain epigenetic bands of $Fe(OH)_3$ in some kinds of sandstone containing much clay. These bands are parallel to the surface or to slits. Or they surround concentrically the openings made previously by roots of plants. With some of these sandstones it is probable that originally a ferrous compound like $FeSO_4$ was equally distributed in them and that on inward diffusion of O_2 oxidation and rhythmic precipitation of $Fe(OH)_3$ took place. Some ores, *e.g.*, a zinc carbonate as described by S. F. Langhin, are supposed to have originated by rhythmic precipitation. But there is the difficulty that before its transformation one component (the ore itself) being already insoluble, could not move in the direction to the inwardly diffusing substance, and therefore a corona of reduced concentration could not be formed.

As M. Watanabe has shown experimentally, metallic sulfides can be easily obtained in strata within jellies. We must still await which of these results can be taken as an explanation of ore deposits, because in these cases a change in external conditions may also have caused layer or strata formation Furthermore, capillary action must also be considered.

Still greater caution must be taken in transferring these facts to conditions in organisms. The closest resemblance may perhaps be to the precipitation of Ca salts in bone formation, which in many cases also occurs rhythmically. In the impregnation of histological preparations with silver compounds, artificial structures are easily produced by rhythmic precipitation. This yields, *e.g.*, with Frommann's recipes, pre-existent artefacts which are not as formerly believed. To make it possible for a macroscopical precipitation to occur rhythmically, the substance being formed must not be too difficultly soluble nor must it be capable of reaching a very high degree of supersaturation. The latter condition is to be assumed for the precipitate, which easily occurs in the form of bands or strata on reduction of $AgNO_3$ by $FeSO_4$ or by photographic developers in a gelatin jelly. The observations made on physical development of silver images also confirm the possibility of a great supersaturation of metallic silver and its ability to diffuse in jellies. On the other hand the solubility and possibility of supersaturation are so very small with AgCl, that none or only microscopically thin bands occur. But there is a method of obtaining even this substance in very thick bands by means of a device. Let a drop of NaCl diffuse in a layer of gelatin jelly containing a little $AgNO_3$. At some distance from the drop place a little precipitated silver chromate. As soon as the ring of diffusing NaCl reaches this powder it becomes changed into AgCl. Instead of NaCl, $Na_2Cr_2O_7$ is set free, which now, on diffusing, once more forms $Ag_2Cr_2O_7$ with $AgNO_3$. This is again reached by the NaCl, changed, and in this manner $Na_2Cr_2O_7$ is continuously set free. The silver chromate is formed in thick bands and the AgCl developing from it is also obtained in the same shape. A soluble dichromate, when added to the NaCl drop itself, acts similarly as a catalyzer for the structure, *i.e.*, as a substance impressing its shape on another one and yet being found afterwards in its original condition.

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* See paper by S. C. Bradford, this volume. J. A.

Owing to the very considerable concentration gradient found in diffusion in jellies, it is probable that there may come into operation the "zones of precipitation" referred to by Prof. A. Lottermoser in his paper, this volume, p. 670.

The next three papers give some other aspects of the behavior of diffusible substances in jellies, whose constituent particles are substantially fixed. J. A.

Banded Precipitates in Porous Media

By S. C. Bradford, D.Sc., The Science Museum, London, S. W. 7.

Under suitable circumstances, precipitates formed by diffusion of reacting solutions into gels, or other porous media, may be deposited in a number of separate bands, or layers, sometimes associated with large spherical aggregates. The density of the precipitates may diminish regularly as the diffusion progresses, until all the hypotonic reagent is exhausted, or there may be periodic variations in the density of the precipitate of any degree, including actual discontinuity, when the precipitate separates in beautiful sharply defined bands with clear interspaces. Figure 1 shows the appearance when $2\ N$ silver nitrate solution is allowed to diffuse into 1 per cent agar gel made $\frac{N}{100}$ to potassium dichromate and $\frac{N}{55}$ to potassium citrate. This curious phenomenon has been recognized as of importance in geology [1, 2, 3, 4, 5] and biology [6, 7] and may be the explanation of the striated and laminated structures to which are due some of the most beautiful colors in Nature.

The first record of the formation of noticeable structures, by the diffusion of precipitating-reagents, appears to have been made in 1855 by Runge,[8] who experimented with precipitates produced in blotting paper. Monnier [9] and Vesque [10] observed that large crystals are formed by slow diffusion of reagents through filter paper and gels, respectively. Ord obtained growth forms and spherites by diffusion of ammonium oxalate and calcium chloride into an isinglass gel. The first systematic study of diffusion in gels was made by Pringsheim,[11] who allowed solutions to diffuse in opposite directions through gelatin gels contained in the horizontal portion of a graduated U-tube. He discovered the important law that, after the formation of a precipitate, diffusion takes place only from the hypertonic into the hypotonic reagent. In several cases Pringsheim observed the formation of two bands, which he thought might be due to dissociation phenomena. Lupton [12] first produced a series of layers, which he did not investigate. But in 1896 Liesegang [13] placed a drop of strong silver nitrate solution on a glass plate coated with moist gelatin containing a trace of potassium dichromate and obtained the remarkable series of rings now so well known. Perceiving the importance of the phenomenon, Liesegang made a series of investigations. He showed that none of the hypotonic reagent is left between the bands, and obtained similar structures with various other insoluble precipitates.

Having inspected Liesegang's "astonishing" preparations, Wilhelm Ostwald [14] suggested that the phenomenon is due to supersaturation. This hypothesis has been supported by Morse and Pierce,[15] who attempted a mathematical analysis, and by Stansfield,[16] Holmes,[17] Lord Rayleigh [18] and Notboom.[19]

The supersaturation theory has been criticized by a number of writers. Bechhold [20] showed that the production of banded precipitates is influenced by the effect of the reaction components on the solubility of the precipitate, and by their coagulating, or inhibiting, effect. Sir J. J. Thomson * supposed that the soluble substances produced by the reaction might act as stabilizers and prevent precipitation in their neighborhood, Moeller[21] suggested that the bands might be caused by structures pre-existent in the jelly, Dreaper[22] obtained bands of copper sulphide in sand, Freundlich and Schucht[23] thought that precipitation might be due to electrolyte-coagulation of sols, and McLaughlin and Fischer[24] supposed that the diffusion might be interrupted temporarily by the momentary formation of semipermeable membranes. Hatschek[25] studied reactions in various gels, including the inorganic gel of silicic acid, and found that the particles of precipitates in gels are usually microscopic spherical aggregates and generally larger than in water. He showed the difficulty of explaining by supersaturation all the complicated phenomena which accompany the formation of banded precipitates and pointed out that if, as Ostwald thought, the silver dichromate is deposited on the ring from the neighboring region, which is supersaturated in regard to this salt, it should be impossible to produce a set of rings in a gel already containing one, or sown with crystals of the insoluble precipitate, which is contrary to fact. Hatschek's view of the inadequacy of the supersaturation hypothesis was endorsed by Wo. Ostwald.[26]

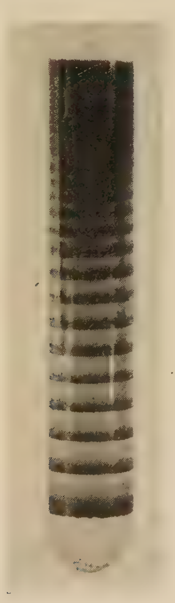

FIG. 1.

Complete mathematical analysis of the supersaturation theory is not easy. Without this it is difficult to decide against it. But only precipitates that are very finely divided occur in the banded form, and the supposition that the precipitate acts, like fine powders are known to do, and adsorbs the dis-

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* In a lecture at the Royal Institution in 1912.

solved substance from the region of gel adjacent, affords a simple explanation [27] of the separation into bands, the effect of the medium and all the numerous accompanying phenomena. It indicates also how to obtain bands of any insoluble substance. It will be seen that the adsorption theory is more complete than the supersaturation theory, and includes the latter.

In the formation of stratified precipitates two distinct problems are involved (1) the mechanism of precipitation and the crystalline form of the resulting precipitate and (2) the density of its distribution. The former is connected with the general problem of solution,* which is still in an unsatisfactory state. By gradual mixing of the reagents a metastable solution of the insoluble substance is formed until the ionic product reaches such a value that instantaneous precipitation occurs.† [28] The metastable limit is influenced by the reaction products and reaction medium, but it is improbable that the particles of the metastable solution are as large as those of a sol, because diffusion [29] is a necessary part of the phenomenon.

By the formation of the precipitate the concentrations of the reacting solutions are reduced, and diffusion gradients are set up towards the place where precipitation is happening. The theory of solution shows that the particles of the insoluble precipitate have very much greater resultant attraction for like particles in the solution in the gel than for more soluble substances, or for the reaction medium. This is the mechanism by which crystals grow. If the precipitate is very finely divided it will have great adsorbing power and reduce appreciably the concentration of the gel in its immediate neighborhood in regard to the insoluble substance. The rate of adsorption will be greater than the rate of diffusion, although solute can reach the narrow exhausted zone only by diffusion. Precipitation will continue until the concentration at the surface of the precipitate of the insoluble substance has fallen to such a very small value that it is in equilibrium with the precipitate under the conditions of the experiment. When this happens, the laws of adsorption indicate that the concentration of the gel in the immediate neighborhood of the precipitate will be much less. The ionic product of the reacting solutions will correspond to this value, and the concentration of the more dilute reagent will be very small indeed. Diffusion of the stronger reagent into this narrow zone will not produce a precipitate, and no further precipitate will be formed until the stronger reagent has reached a point where, with greater concentration of the dissolved substance, the ionic product has risen not merely to the solubility product, but to the metastable limit. At this point the formation of a fresh band will commence and the adsorption of the reaction components from both sides of the band will take place. Although the ionic product may fall below the solubility product only in a very narrow zone, the distance between the bands may be much greater.

If the specific surface of the precipitate is less, its adsorbing power may not be sufficient completely to prevent precipitation in the adjoining zone. Then the hypotonic reagent will be more or less exhausted according to the grain size of the precipitate. If the precipitate is finely divided, the adsorption will be greater, the concentration less in the adjacent zone and here, by von Weimarn's [30] formula,* the precipitate will be coarser. This coarser precipitate will cause less reduction of the concentration in its neighborhood, with the formation of a finer precipitate, and the cycle will be repeated.

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* See "The Sol-Gel Transformation," this volume, p. 751. J. A.

† Actually the velocity of precipitation increases rapidly with the ionic product until the velocity becomes instantaneous.

Many facts support the view that the precipitate acts as an adsorbent. The strong adsorption of salts with common ions by difficultly soluble substances is well known. In gels containing strongly colored substances (*e.g.*, $N/20K_2CrO_4$ agar gel treated with $N/5Pb(NO_3)_2$ solution, see Fig. 2) the exhaustion of the solute from the zone adjacent to the precipitate is strikingly demonstrated. Moist precipitates and fine powders, placed upon gels in test-tubes, exhaust colored solute from them, quickly producing narrow colorless zones immediately beneath. With fuller's earth and clay on gels containing deeply colored substances, such as night blue and magenta, the effect is remarkable, see Fig. 3.

The more colloidal precipitates, like manganese sulphide (produced by diffusion of half molar manganese sulphate solution into 1 per cent agar gel containing 0.25 per cent of liver of sulphur) sometimes form large spherical aggregates, whose shape indicates equal attraction of nutrient material from all directions. When one of these aggregates commences to form in a zone, where a band subsequently appears, a concentric spherical cavity, free from precipitate, is left between the aggregate and the new band. An apparent exception to Pringsheim's law may be caused if the precipitate adsorb the strong reagent much more than the weaker one. With $\frac{M}{30}$ K_4FeCy_6 diffusing against $M/50CuSO_4$, after the formation of about 1 cm. of precipitate, consisting of very tiny spherical particles with marked density variations 0.5 to 1 mm. in length, the precipitate will grow about 3 mm. more backwards, indicating diffusion in the direction of the ferrocyanide. When precipitation ceases there is no copper in one liquid, but still some ferrocyanide in the other.

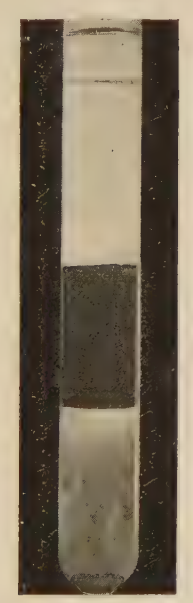

Fig. 2.—Adsorption of potassium dichromate by precipitation of lead chromate.

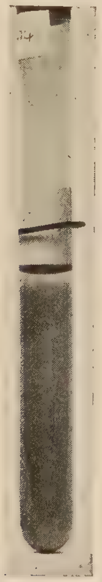

Fig. 3.—Adsorption of night blue by fuller's earth.

If the precipitate be too dense, or too colloidal, the diffusion of the hypertonic reagent may be hindered so much that dissolved substance can diffuse more quickly through the exhausted zone and there will be no separation into bands. The remedy is to make the precipitate more permeable. With lead chromate this can be done by reducing the concentration of the reagents. The opposite case occurs when the precipitate is too coarse to exert sufficient adsorption. The most well known cases of this effect are the chromate and dichromate of silver, which develop beautiful brick-red rings in gelatin, but only large black crystals in agar, see Fig. 4. This is a good example of the rule that the form of the precipitate is influenced by the nature of the reaction medium. The non-formation of bands in agar is due to the lack of specific surface. The reason why these salts have great specific surface in gelatin and very little in agar is part of the altogether separate problem of the crystalline form of the precipitate. Von Weimarn's theory shows how to increase the specific surface. It can be done by decreasing the solubility, or by increasing the excess concentration before precipitation occurs. Salts of polyvalent acids increase enormously the metastable limit of silver chromate and dichromate. By adding soluble citrates, the excess concentration of the insoluble substance, and consequently the specific surface of the precipitate, can be increased to any desired degree. As the grain size decreases, the banding appears, grows more marked and then completely discontinuous, and finally the precipitate becomes too colloidal to form bands. The most beautiful result is obtained with 2 $N/AgNO_3$ solution poured on 1 per cent agar gel made $N/100$ to K_2Cr_2O, and $N/55$ to $K_3C_6H_5O_7$, see Fig. 1. These principles appear to be applicable to the production of bands of any substance sufficiently insoluble.

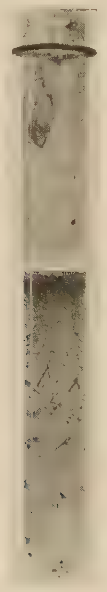

FIG. 4.—Crystals of silver chromate in agar.

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A paper by St. Leduc will appear in Vol. II, Biology and Medicine. J. A.

Recently Wo. Ostwald has suggested that the stoppage of precipitation at the end of a band is due to the formation of excess of one of the soluble components of the reaction, and that, when this diffuses away, precipitation begins again. He adds that most reactions, which produce good stratifications, are "limited reactions" that cease when sufficient of the soluble by-product has accumulated, and that barium sulfate, the precipitation of which is typically complete, proved quite unsuited for producing good stratifications. However, the writer has obtained good stratifications of barium sulfate, and extensive experimental investigation indicates that bands can be obtained of any comparatively insoluble substance. S. C. B.

Reactions in Gels

By Harry N. Holmes, Professor of Chemistry, Oberlin College,
Oberlin, Ohio

GELS

When a substance is formed in a liquid in which it is insoluble or when conditions attending a substance in solution are so changed as to decrease greatly its solubility, a precipitate is formed, crystalline or amorphous as the case may be.

When the precipitated substance holds much of the liquid in a more or less solid mass it is referred to as a "gel" or as a "gelatinous precipitate." A gel or, as it is often termed, a "jelly," usually holds all the liquid at first, although free liquid may separate later. In any event the gel has greater rigidity and elasticity than the gelatinous precipitate. Gel structure is more uniform. However, any distinction between the two is rather arbitrary.

Some distinction should be made between "true gels" of the agar, soap or gelatin type, in which the interlacing fibers undoubtedly adsorb much water (or other liquid), and the "false gels" of the caffeine type, in which coarse, interlacing, needle-like crystals entangle considerable water without actually adsorbing it on the surfaces of the caffeine crystals. Of course, there must be gels of every gradation between these two extremes.

Von Weimarn considered his best transparent gels as made up of ultramicroscopic crystals.*

Diffusion.

The comparative ease of diffusion through gels indicates continuous channels of rather dilute solution. This is in accord with Bütschli's theory of a honeycomb structure, although a filamentous or brush-heap structure will explain the facts just as well. J. M. von Bemmelen considered gels to be two-phase systems—a more concentrated solution as a network of cell walls, enclosing a more dilute solution of the same substance.

Graham overstated it, however, when he announced that diffusion of salts through gels was almost as rapid as through water. This is true only for very dilute gels. Diffusion in the more concentrated gels is comparatively slow (Bechhold and Ziegler[1]). This regulation of the rates of diffusion of solutions by gels has great influence on the formation of crystals, and, in some instances, on the nature of the reaction. The permeability of a gel may be greatly affected by substances diffusing through it so that progressive changes may take place. Bechhold and Ziegler showed that the presence of alkali, sulfates, alcohol, glycerol or glucose retard diffusion in gelatin, while chlorides, iodides, and urea accelerate it.

Geology.

The influence of certain gels—or jellies—on crystal growth is illustrated by many crystalline minerals. It is very probable that gelatinous silicic acid was the ancestor of quartz (except igneous quartz). In fact, when the Simplon tunnel was dug, G. Spezia[2] found a vein of white, gelatinous silica in the depths of the mountain. Such material by gradual dehydration became hard silica rock. In the gelatinous medium reactions took place under conditions favoring the formation of crystalline veins. For example, the reduction of gold salts produced crystals of gold, veining the gel which later became quartz. A convincing part of this development can be reproduced in the laboratory. To the geologist a working method of duplicating many such processes of nature must be of great value.

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* See paper by P. P. von Weimarn, this volume, p. 27. J. A.

Hatschek and Simon[3] reduced gold salts in silicic acid gels by the use of oxalic acid, ammonium formate, ferrous sulphate, sodium sulphite, carbon monoxide, sulphur dioxide, hydrogen, ethylene, etc. When illuminating gas was used as a reducing agent a black deposit of carbon always appeared mixed with the gold. Since graphite sometimes occurs with gold in quartz veins, this experiment is suggestive.

Hatschek's usual method[4] of work was to make a 5-20 per cent gelatin gel or a 1-5 per cent agar gel containing, for example, a small amount of potassium dichromate. This was allowed to solidify in a test-tube and covered with a solution of silver nitrate. The silver ion slowly diffusing down into the gel reacted with the dichromate ion to form silver dichromate in small crystals. In 1911 Hatschek reported these crystals 0.5 mm. long in 10 per cent gelatin, lead dichromate 0.03 mm. long in 2 per cent agar; lead chloride 2 mm. long in agar; barium carbonate 0.1 mm. long in 5 per cent gelatin; potassium sulphate 0.2 mm. long in 5 per cent gelatin. He also prepared a number of other crystalline compounds such as lead iodide, lead sulphate, lead chromate, calcium sulphate and barium silicofluoride. Later he used silicic acid gels as the media for diffusion and obtained larger crystals. In 1913 he reported lead chloride crystals 15 mm. long.

His reduction of gold chloride in silicic acid with oxalic acid yielded beautiful crystalline gold and, by varying the conditions, colored colloidal gold.

Simon[5] grew the well known "lead tree" in a silicic acid gel containing lead acetate. A bit of zinc or tin was pressed into the top of the gel. Holmes found that if the gel is about 0.02 N with respect to lead acetate a splendidly branching tree grows and may be handled roughly since it is supported on all sides by a solid.

Pringsheim[6] states that when two salt solutions diffuse into a gel in opposite directions the reaction does not proceed beyond a thin film if the solutions are isotonic. A hypertonic solution continues to diffuse into a hypotonic and any precipitate formed is deposited in the latter. In accord with this idea Hatschek often added indifferent substances to the solution on top of the gel in order to ensure reaction below the gel surface.

Dreaper[7] dispensed with a gel as a medium for reactions and used a single capillary tube. For example, a capillary tube filled with 3 per cent lead acetate was immersed in 5 per cent hydrochloric acid. Crystals of lead chloride nearly 1 mm. long formed in the capillary. Sand in wide tubes functioned the same as a single capillary. Dreaper considered relative rates of diffusion and concentration of the incoming solution to be the determining factors.

De Schulten,[8] by the slow admixtures of extremely dilute solutions of barium chloride and sulphuric acid, obtained crystals of barium sulphate that in a month measured 5 mm.

Braun[9] believed that certain phenomena attending the formation of sulphides and the deposition of copper in capillary spaces previously noted by A. C. Becquerel, are of an electrochemical nature as Becquerel had suggested. These phenomena are partly dependent, according to W. Ostwald, on the semipermeability of precipitated membranes.

Cornu's[10] great series of papers on the significance of gels in geology are an important part of the literature.

With Cornu's work must be mentioned the papers by Krusch[11] and those of Hatschek and Simon.[12]

Selective adsorption of the base from salt solutions is, doubtless, the first step in the deposition of certain minerals. Kohler[13] explains some copper ores in this way, referring to kaolin as the adsorbing material. J. M. von Bemmelen[14] believed that aluminosilicate hydrogels in general were strong adsorbents.

H. N. Holmes[15] observed that the use of silicic acid gels offered the best laboratory parallel to the gel processes in Nature. His methods of preparing such gels and of using them as reaction media may be of interest to geologists. He found it convenient to mix equal volumes of solutions of sodium silicate and some acid, pouring the water glass into the acid and mixing quickly and thoroughly. Before the silicic acid set to a solid, one of the reacting salts was mixed with this solution which was then poured into test-tubes. After the gel set the other salt solution designed to react with the first, was poured on top. The solution on top should have a greater osmotic pressure than the gel to ensure reaction within the gel instead of above the surface. Hatschek, as stated before, often added indifferent substances to the solution on top of the gel.

The water glass used was a commercial grade known as "water white" with a density of 1.375. The ratio of the Na_2O to the SiO_2 was 1 : 3.5. When diluted to a density of 1.06 and titrated against hydrochloric acid using phenolphthalein as an indicator, it was equivalent to 0.51 N acid. With methyl red as indicator the normality was 0.57.

This particular water glass was used at the 1.06 density for many experiments because with weaker solutions the silicic acid set too slowly. With this concentration an equal volume of N acetic acid was suitable for most of the experiments. Such a gel set over night and contained a small excess of acid. It was reasonably clear. This rather arbitrary selection really marked the lowest concentration limit for working convenience. Acetic acid 0.75 N serves as well and gives less excess acid. Several other acids were used for special purposes, for the time of set varied with the acid. A partial list follows:

Sodium Silicate Mixed with Equal Volumes of Acid

	1.06 Density Sodium Silicate		1.12 Density Sodium Silicate	
Acid	Gel Set in 2 to 3 Hours	Gel Set in 8 to 10 Hours	Gel Set in 2 to 3 Hours	Gel Set in 8 to 10 Hours
Hydrochloric	0.55 N	0.6 N	1.2 N	4.0 N
Nitric	0.55 N	0.6 N	1.2 N	4.0 N
Sulphuric	0.55 N	0.6 N	1.2 N	6.0 N
Phosphoric	0.75 N	1.5 N	2.5 N	3.0 N
Formic	0.70 N	0.9 N	1.5 N	2.0 N
Acetic	0.80 N	1.2 N	2.2 N	3.5 N
Citric	1.00 N	1.2 N	2.5 N	3.0 N
Tartaric	0.80 N	0.9 N	2.2 N	——
Lactic	1.00 N	1.2 N	2.5 N	3.0 N

Pouring the mixture before it solidifies into the bend of a U-tube gives the experimenter excellent control of conditions. The two reacting solutions poured separately into the arms of the U-tube slowly diffuse through the gel and meet, often forming a sharp precipitation band. Any amount of either solution can be used in this method.

The mixture of water glass and acid may be dialyzed to free it from excess acid and salts. Addition of very little ammonia then sets the gel. However, it is neither necessary nor always desirable to dialyze out the acid and salts. Their influence on crystal formation or development of banding is beneficial in most instances.

Doryland suggested that a mixture of water glass and just enough acid to make a neutral solution would set to a gel in minimum time. Traube and Kohler[16] came to a similar conclusion in regard to the effect of acids and bases on gelatin. This led Holmes to make basic gels by using less acid than enough to neutralize the sodium silicate. In this way a very profitable field of investigation was opened up. Basic salts, for example, may not be studied in gels containing excess acid. A mixture of equal volumes of 1.06 density water glass and 0.5 N acetic acid is very slightly basic and sets in about three minutes. Other water glasses must be titrated to get similar figures.

Some of the results obtained by Holmes are given below. Hatschek had previously prepared crystalline gold in a gel made by mixing sodium silicate with hydrochloric acid. However, Holmes found that gold in a beautifully crystalline condition was best prepared by mixing equal volumes of a water glass, 1.06 density, and 3 N sulphuric acid, adding 1 c.c. of 1 per cent gold chloride to 25 c.c. of the mixture and, after solidification of the gel, covering with a solution of 8 per cent oxalic acid.

Startling rainbow bands of red, blue and green colloidal gold mixed with scattered crystals resulted when the water glass was of 1.16 density. Both methods work readily and give better results than any yet recorded.

Perfect tetrahedrons of copper were secured by using 1 per cent hydroxylamine hydrochloride to reduce dilute copper sulphate in a silicic acid gel. Peculiar aggregates of tetrahedrons similar to those found in copper deposits in nature were also observed.

Lead iodide in perfectly hexagonal plates 5 mm. wide and golden fern-like growths 8 cm. long were formed in silicic gels by allowing potassium iodide to diffuse into gels containing lead acetate.

Red mercuric iodide in 2 cm. needles or, in smaller crystals, banding in as many as forty regular bands in a distance of 8 cm. was obtained by the diffusion of a mercuric chloride solution into a gel silicic acid gel containing potassium iodide. With certain concentration conditions yellow crystals formed in front of the red needles and were finally changed into the red mercuric iodide. Soluble chlorides exerted a striking influence on the size, form and arrangement of the mercuric iodide crystals.

Magnificent red-black crystals of a basic mercuric chloride resulted when a saturated solution of mercuric chloride diffused into a silicic acid gel of slightly basic reaction. In a very slightly basic gel these crystals were grouped in a remarkable series of bands. The presence of a little glucose exerted a marked influence, changing the color and developing over one hundred compact bands in a distance of 8 cm.

Silver sulphate crystals appeared in less than one hour when N silver nitrate diffused into a silicic acid gel made by mixing equal volumes of 1.06

density water glass and 3 N sulphuric acid. In a few days orthorhombic slabs 3 cm. long developed. If enough potassium dichromate to make the whole gel 0.1 N molar with respect to this salt was present the long slabs were a beautiful clear red. In the presence of excess silver nitrate near the surface of the gel silver chromate was formed, and since silver chromate and silver sulphate are isomorphous, red mixed crystals resulted. The color of the crystals was made any depth of red by varying the concentration of the potassium dichromate in the gel. Farther below the surface of the gel the silver nitrate became less concentrated and triclinic crystals of the red-black silver dichromate appeared. In time they grew to a size of 3 cm.

Dreaper [17] held that the most important feature of the favorable influence of gels on reactions forming crystals was the capillarity of the gel structure. He substituted fine sand and even a single capillary tube for the usual gels, and secured crystalline products. Holmes secured good crystals of silver dichromate in a U-tube partly filled with flowers of sulfur and with a solution of silver nitrate in one arm and a solution of potassium dichromate in the other. Barium sulphate and alundum powder served much better than sulphur as substitutes for a gel. In fact the results with alundum were startling. Silver dichromate formed in flat needles 1 cm. in length.

Without doubt any compact mass of insoluble discrete particles with proper size capillaries will function as a gel in favoring the formation of crystals. Other influences may be present in a true gel. Adsorption, pressure and solubility effects may greatly influence the capillary space results. A rather amorphous insoluble compound first formed by the meeting of two reacting substances in a relatively narrow channel may so further regulate the rates of diffusion as to give time for crystal formation of more of the same insoluble compound. In this suggestion the geologist may possibly find an explanation of the marked crystalline nature of some mineral veins. The pathologist, too, may obtain some light on the accumulation of crystalline deposits in animal tissue.

To test the theory, the mouth of a small specimen tube was covered with a sheet of goldbeater's skin held on firmly with a rubber band. The tube had first been filled with a solution of 0.1 N potassium iodide. Care was taken to leave no air bubbles on the under side of the membrane and to rinse the outside of the tube. The tube was then immersed in a small beaker of saturated lead acetate solution. At once an almost amorphous precipitate of lead iodide appeared on the under side of the membrane and in less than a minute crystals of lead iodide fell in a beautiful gleaming shower, rapidly increasing in amount. It is very easy to secure gleaming crystals of lead iodide by cooling its hot solution but in this experiment the solutions were cold. Mixing the same solutions in a test-tube without the use of a membrane a yellow powder results.

When the more concentrated solution was placed inside the specimen tube, the crystals formed on the upper surface of the membrane. This is in accord with the osmotic difference rules of Pringsheim. With less difference in concentration of the reacting solutions the reaction was much slower.

Separating solutions of silver nitrate and the potassium dichromate in this way it was a simple matter to make a gram or two of brilliant crystals of silver dichromate settling to the bottom of the tube. Possibly this method may be of some use in the preparation of pure compounds, since the crystals are not mixed with an annoying gel. Other thin semipermeable membranes serve. Parchment paper is good but goldbeater's skin is most suitable.

In a number of experiments it was observed that at first a rather amorphous or, at least, fine-grained precipitate formed on the surface of the original membrane, thus forming a new membrane of different capillary structure, which exerted a marked influence on rates of diffusion. The result of checking the rates of diffusion of the reacting substances was to give time enough for the growth of minute particles to crystalline size.

Barium sulphate is most annoying in quantitative analysis because of its tendency to form slow-settling colloidal suspensions. It seemed an interesting experiment to precipitate it by the diffusion cup method and observe the rate of settling. I believed that if I placed a dilute solution of a sulphate inside the specimen tube, covered it with a goldbeater's skin touching the surface of the solution and immersed the tube in a more concentrated solution of a barium salt that the barium sulphate formed on the under side of the membrane would be of much larger size crystals than usual and would settle rapidly. It did. Some modification of this experiment may possibly be applied to the determination of sulphates.

To carry the theory further, the only need of the goldbeater's skin is to prevent sudden wholesale mixing of the solutions and mechanically sustain the rather amorphous precipitate first formed which then functions as the real active membrane. This theory is not universal in its application, for in gels excellent crystals of a number of substances form without the appearance of a preliminary compact layer of precipitate. In these instances only the gel functions in regulating diffusion. The theory does apply, however, in the absence of a gel and in all instances where a compact precipitation band is formed.

John Johnston's [18] method of preparing crystals of increased size by the slow diffusion of two reacting solutions in a large volume of water at two widely separated points supports the theory above given. De Schulten's experiment described earlier in this paper is somewhat similar to Johnston's.

A variety of gels may be used to influence the formation of crystalline products, but in general it may be stated that larger crystals form in silicic acid gels than in agar and gelatin. In the latter there is a marked tendency to favor the formation of spherulites. Probably the protective colloid effect of gelatin and agar is an important factor, as well as the elasticity of the gel. At any rate the effect of silicic acid gel on crystal formation may be greatly changed.

A very little gum tragacanth in a silicic acid gel greatly hindered crystallization of lead iodide, in fact caused the appearance of spherulites. Under similar conditions gum tragacanth (and other protective colloids) caused silver acetate to form in twisted, fantastic shapes instead of in the usual straight white sheets.*

Glucose, gelatose, and salts also exert marked influence on crystal formation in gels. Liesegang [19] boiled 20 per cent gelatin several days and added a little of this to gelatin containing potassium dichromate. The gelatose formed prevented crystallization of the dichromate on drying. Such a boiled solution of gelatin does not permit the separation of ice crystals at — 10°.

Perfect sugar crystals 2 cm. long have been observed in fruit jellies.

Ernest Marriage [20] studied the arrangement and size of lead iodide crystals in fruit gels and jams. The various fruit jellies and jams influenced the precipitation of lead iodide in different ways and use was made of this fact in detecting adulteration of commercial products.

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* See also this volume, p. 619. J. A.

Dry cells discharging on short intervals service develop colorless sheets several cm. long of $ZnCl_2 . 2NH_3$ next the zinc wall of the battery. The gelatinous paste in this part of the cell regulated the diffusion of the zinc chloride and ammonia formed by the discharge of the cell.

Shulansky and Gies[21] observed that "in the putrefaction of meat, crystals of ammonio-magnesium phosphate appear early and accumulate rapidly" due to bacterial activity. This paper and a similar one by Perlzweig and Gies may have some bearing on the subject because of the hydrated colloid nature of animal tissue.

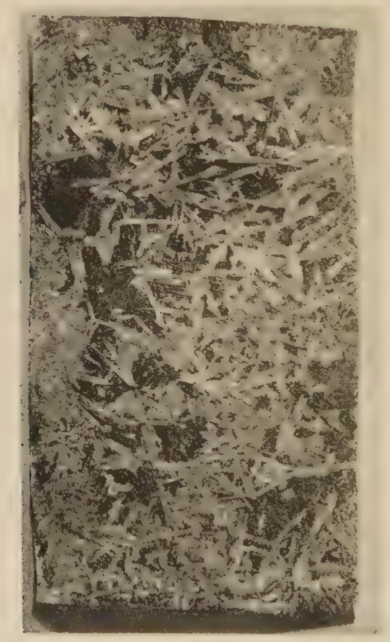

FIG. 1.—Crystals of $ZnCl_2.2NH_3$ next the zinc wall of a dry cell.

In fact the pathologist may well consider the possible parallel between the gel reactions here described and those that occur in the gel tissues of the body.

S. E. Sheppard[22] in the first of a series of monographs on the theory of photography, offers many striking photographs of crystals of silver bromide in gelatin. He observes, "Hence we must regard sensitive photographic emulsions not only as suspensions of silver halid crystals in gelatin, but also as a probably very much more complex suspension of gelatin in crystalline silver halide."

Banding.

Rhythmic banding of precipitates was first observed and recorded by Liesegang, hence the name "Liesegang's rings." * His original experiment dealt with the rhythmic precipitation of silver chromate in gelatin. A solution of silver nitrate was poured on a solid gel containing dilute potassium chromate.

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* See paper by R. E. Liesegang, this volume, p. 783. J. A.

The precipitate of silver chromate formed was not continuous but marked by gaps or empty spaces at regular intervals.

Holmes [23] studied the banding of mercuric iodide, gold, copper chromate, cuprous oxide, and other substances in silicic acid gels.

Mercuric Iodide.

A tube of silicic acid gel (from mixing equal volumes of 1.06 density water glass and N acetic acid) was made 0.1 N with respect to potassium iodide and covered with 0.5 N mercuric chloride. In a few days bands of red crystalline mercuric iodide began to appear. These bands were not sharply marked for the first cm. or two below the surface of the gel but below that depth were excellent. In some tubes there were 40 bands rather sharply marked in a distance of 8 cm. The spaces between the thin disks contained many scattered crystals.

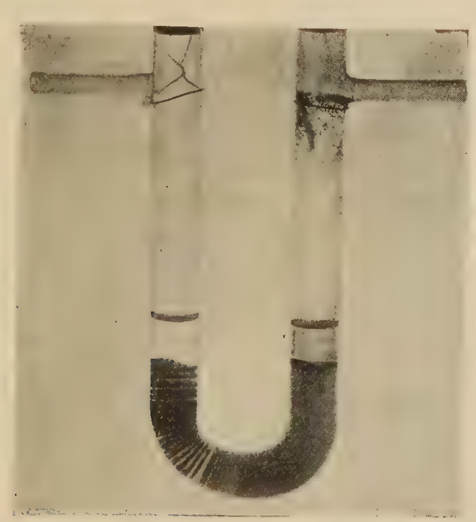

FIG. 2.—Bands of mercuric iodide in a silicic acid gel.

In a U-tube with a gel filling the bend, 0.5 N mercuric chloride in one arm and 0.1 N potassium iodide in the other, the sharp red bands of mercuric iodide followed the curve like ranks of soldiers pivoting in regular formation. The excess of mercuric chloride diffusing into the gel reacted with the red mercuric iodide forming a soluble colorless double salt, leaving the gel somewhat clearer where the red bands had been. This gave the appearance of shadow bands following in the rear.

The presence of glucose in the gel made the bands very much sharper. Sodium chloride, on the other hand, diminished the tendency to band and in sufficient concentration prevented it altogether. In a gel of the composition described above but containing an added 10 per cent of sodium chloride, the mercuric iodide formed, not in the usual red needles, but in much larger crystalline aggregates and very few bands appeared. The crystals were scattered in an irregular way. The addition of sodium chloride to the amount of 25 per cent of the weight of the gel caused the appearance of still larger widely scattered crystalline aggregates. Neither needles nor bands were in evidence. Since a gel made from sodium silicate and hydrochloric acid contains considerable soluble chloride no sharp banding of mercuric chloride could be expected under such conditions. This may explain why earlier investigators in this field failed to record the beautiful examples of banding possible with mercuric iodide.

Copper Chromate.

The banding of copper chromate in a silicic acid gel of very slightly basic reaction affords the best material for a detailed study of the phenomenon. Gold banding is often more beautiful but the remarkable sharpness of the layers of copper chromate and the perfect clearness of the gaps excel all other examples.

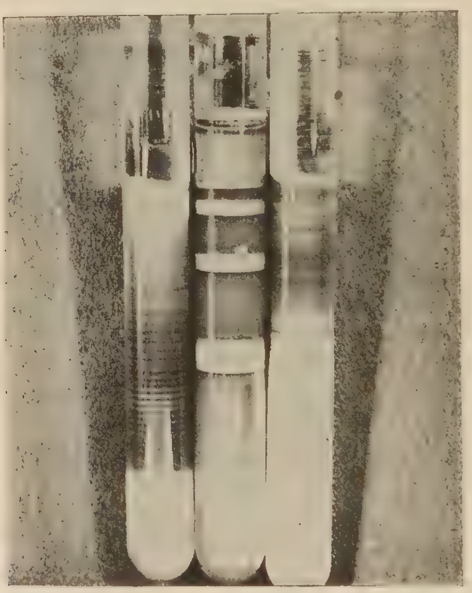

FIG. 3.—Bands of copper chromate in a silicic acid gel.

A gel from mixing equal volumes of 1.06 density water glass and 0.5 N acetic acid was made 0.1 N with respect to potassium chromate (before solidifying) and was later covered with 0.5 N copper sulfate. In a day or two bands of apparently amorphous copper chromate formed. The first layer was often rather deep, one cm. or more, then a clear gap with no trace of a precipitate of copper chromate, below that a much thinner band, more gaps and bands, the gaps widening steadily. These relative distances varied not only with the initial concentrations of the reacting solutions but also with the volumes of the potassium chromate solution in the gel and the copper sulfate solution above. It is, of course, apparent that these relative volumes greatly influenced the rates of decrease in the initial concentrations. The distances were also influenced by the substitution of other acids for acetic in making the gel. An increase in the excess of sodium silicate with its resulting alkalinity brings the bands of copper chromate closer together.

Addition of sugar to the usual gels made the bands thinner. Urea had the opposite effect. The influence of gravity was shown by corking tubes and inverting. The bands were irregular and made up of crescent-shaped fragments.

Cuprous Oxide.

With a basic gel very different results were obtained. Glucose, a few grams to 25 c.c., was mixed with a 1.08 water glass-0.5 N acetic acid gel and covered with 0.5 N copper sulphate. After a few months close bands of rather amorphous cuprous oxide extended down the gel for a distance of about 12 cm. At first the bands were yellow, but as they aged they turned to a dull red. At one time both colors were in evidence, the newer bands yellow. Near the surface of the gel a blue deposit of cupric hydroxide formed. This reaction is suggestive of Fehling's test for glucose.* Of course no copper complex is used here but evidently slow diffusion permits the reduction from cupric hydroxide to cuprous oxide.

It has been suggested that this method gives opportunity for studying a reaction in its various stages. The control of concentrations and the rates of diffusion pave the way.

Gold banding has been described earlier in this chapter. These bands have been obtained before, but Holmes found the use of sulfuric acid in making the gel a very great improvement. Using hydrochloric acid, the colored bands were quite inferior. With acetic acid instead of sulfuric no bands appeared, but the gel was colored uniformly with violet-blue colloidal gold. However, loading an acetic acid gel with considerable sodium sulfate developed a few shadowy bands. Evidently the influence of sulfates is a factor of importance.

Davies[24] in repeating the experiments of Holmes showed that when diffusion and reduction take place in the dark only the larger particles of yellow gold crystals are produced. He secured the rainbow bands of colloid gold only in changing light. In Davies' opinion light of short wave length is responsible for catalyzing the formation of colloidal gold in silicic acid gel.

Theories of Banding.

The experimental evidence given above justifies the advancement of a more detailed theory of rhythmic banding. For the clearest illustration consider the copper chromate banding.

The gel (a silicic acid gel of slightly basic reaction) contains a dilute solution of a chromate and above it in the tube a solution of a copper salt. The copper ions diffuse into the gel, meet the chromate ions and form a layer of insoluble copper chromate at the surface of the gel. The chromate ions immediately below this precipitation zone diffuse into this region now depleted of chromate ions and meet the advancing copper ions thus thickening the layer of copper chromate. According to Fick's law of diffusion the rate of diffusion is greatest where the difference in concentration of the chromate ions in two contiguous layers is greatest, that is, just below the front of this thickening band of copper chromate. As a result the region near the band decreases in concentration of the chromate ions faster than does the space below. Finally the copper ions have to advance some distance beyond the band to find such a concentration of chromate ions that the solubility product of copper chromate may be exceeded and a new band formed. This repeats again and again.

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* Similar color differences appear when making the Fehling test in sugar-containing urines, due to the presence of protectors, *e.g.*, albumin (M. H. Fischer). J. A.

Not all bands are made up of dense layers. A notable exception is basic mercuric chloride in a very slightly basic gel. The gleaming, feather-like crystals of this salt were sometimes rather widely scattered yet arranged in distinct layers. Rarely were the gaps between these bands free from crystals.

Liesegang's "dead space" experiment [25] confirms the theory advanced above. He filled a glass tube (open at both ends) with gelatin containing 10 per cent of sodium chloride. This tube was then immersed in a solution of silver nitrate which diffused into the gel from both ends of the tube precipitating silver chloride in two bands. However, these two bands of silver chloride did not meet in the middle of the tube. A clear dead space remaining in the center of the tube contained no sodium chloride at all. The salt originally there had diffused away in opposite directions. A dead space was not formed when a gel containing a nondiffusing substance such as albumin was immersed in metaphosphoric acid.

Ostwald [26] held that the silver chromate of Liesegang's original experiment formed a supersaturated solution. When crystallization started at any given point, the excess beyond that required for saturation migrated to the points where crystals were forming. By repetition of this process gaps and bands were produced.

Bechhold [27] advanced the theory that the precipitate of the bands is slightly soluble in products of the reaction and hence that new bands can form only in regions were the concentration of such products has sufficiently fallen off.

Bradford [28] holds that rhythmic banding is due to gradual adsorption of the solute in the gel by the growing precipitate.*

A variant on the formation of crystals *in* gels is the formation of crystals *by* gels.

Deiss [29] prepared a gel of $MnHAsO_4$ by mixing equal volumes of 10 per cent solutions of $MnCl_2$ and KH_2AsO_4. On standing three months rose-colored crystals of the same composition as the gel separated.

Hatschek [30] observed a similar change from gel to crystals in the case of an alcoholic gel of camphorylphenylthiosemicarbazide.

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The Crystallization of Sulfur in Rubber *

By Herbert Arthur Endres

When sulfur crystallizes from solution in the presence of a viscous medium the latter offers considerable resistance to the forces of normal crystal growth, thereby causing many very interesting transformations to take place. Flett[1] and Alexander[2] have studied these phenomena in the case of sulfur crystallizing from a mixture of carbon disulfide and Canada balsam by evaporation of the solvent. Similar transformations are exhibited when sulfur crystallizes from a mixture of benzol and rubber or from rubber itself, for in this case the viscous medium is also a sulfur solvent and the changes continue after the benzol has evaporated.

A study of these transformations was made in connection with an investigation carried out in an effort to gain some insight into the mechanism of the process by which the sulfur efflorescence commonly found on rubber goods is formed.[3] The systems sulfur-benzol, sulfur-benzol-rubber, and sulfur-rubber were investigated. The sulfur transformations were studied microscopically in thin rubber films prepared on microscope slides by the evaporation of smears of rubber and sulfur mixtures dispersed in benzol. This is a very convenient method of obtaining thin rubber sections. To determine the effect of benzol the crystallization of sulfur from benzol was first studied, then introducing rubber, the crystallization of sulfur in a rubber-sulfur-benzol mixture. Finally eliminating benzol, a study was made of the transformations which sulfur undergoes when crystallizing from solution in rubber.

CRYSTALLIZATION OF SULFUR FROM BENZOL

Sulfur can be caused to separate from solution in benzol in several different forms, depending upon the conditions. The most common of these are the rhombic crystalline and the intermediate super-cooled globular. When a drop of a solution of sulfur in benzol is allowed to evaporate slowly on a clean microscope slide and submitted to microscopic examination, the larger part of the sulfur is seen to crystallize directly into rhombic crystals. Some small globules of liquid super-cooled sulfur are formed at the same time, but if the solvent is evaporated sufficiently slowly, these for the most part will deposit on the crystals formed and the latter will then grow at the expense of the globules. If, however, the solvent is rapidly evaporated, as by passing a current of air over a thin film of the solution, numerous globules will be formed and the sulfur will be deposited as such. In this way it is possible to obtain practically all of the sulfur in the super-cooled globular condition. The yield of globular sulfur is therefore determined by the rate at which the sulfur is separated from solution, *i.e.*, the rate of evaporation of the solvent. When the rate of separation exceeds the rate of crystallization, super-cooled globular sulfur results.

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* Based on an investigation carried out at the Research Laboratories of the Goodyear Tire and Rubber Co., Akron, Ohio.

It has been stated that sulfur dissolved in benzol is largely colloidal[4] and there is every reason to believe that the super-cooled globules, deposited on evaporation of the benzol, are formed from colloidal sulfur by coalescence, as is the case when hydrogen sulfide and sulfur dioxide react in water or benzol solution or when solutions of alkali thiosulfates are acidified. The latter process can be observed microscopically by allowing a drop of each of the solutions to run together on a microscope slide. The mixture gradually becomes opaque due to the separation of colloidal sulfur globules throughout the mass which, when examined with dark ground illumination, are seen to be in rapid Brownian motion. These globules then rapidly grow and coalesce until they are plainly visible under low magnification. The large globules then settle out of suspension and solidify. Sulfur globules formed by the above described methods have been examined under a polarizing microscope and found to have no effect on polarized light. They are therefore structureless * and do not consist of sulfur in a crystallized state.

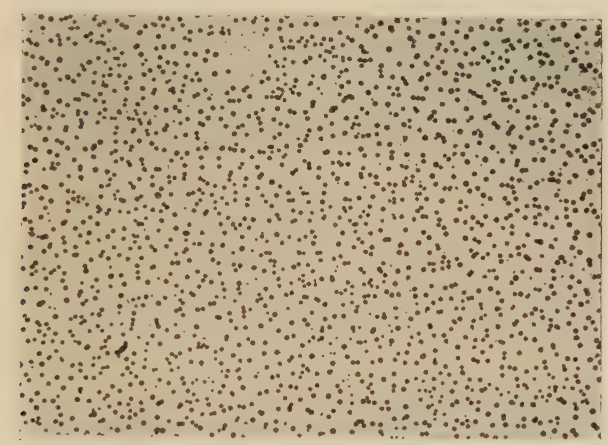

FIG. 1.—Globules of super-cooled sulfur formed in rubber. Mag. 65 diameter on all.

Crystallization of the sulfur globules can be initiated by the introduction of a small quantity of the solid phase; by shock, or other mechanical stimulus. They then become solid masses of crystalline sulfur as shown by microscopic examination and their effect on polarized light.

CRYSTALLIZATION OF SULFUR IN A RUBBER-SULFUR-BENZOL MIXTURE

When sulfur separates out of solution in a rubber matrix, as in the case of sulfur-benzol-rubber dispersions, the system is continuous, and any globules then formed are in a rubber mass which is saturated with respect to this form at the prevailing temperature. Normal crystallization can then take place after the benzol has evaporated, the rubber serving as a solvent for the sulfur through which it diffuses and then deposits on any crystal centers formed.

A series of thin dispersions was prepared in benzol from rubber-sulfur mixings containing from 4 to 10 per cent of sulfur. Thin films of these

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* This simply means structureless to this test. It is probable that the X-ray spectrometer will show the presence of very tiny crystal groups, which surface tension unites into globulites. J. A.

showed no sulfur particles when examined under the microscope, the sulfur all being in solution. As the solubility of sulfur in rubber at room temperature is about 1 per cent, the largest part of the sulfur was dissolved in the benzol.

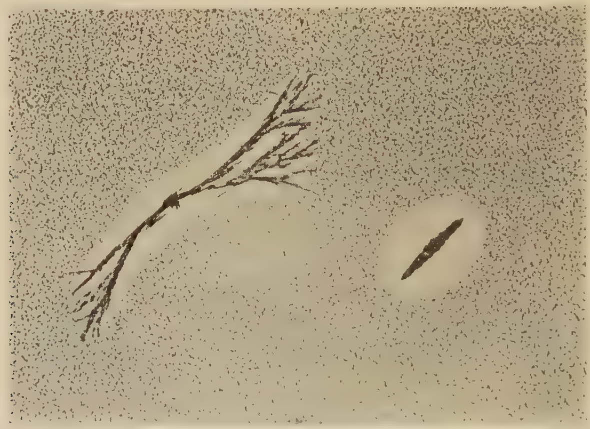

Fig. 2.—Rhombic and dendritic sulfur crystals growing in rubber at the expense of liquid sulfur globules.

On evaporation of the benzol the sulfur held by it separates out in globular form to a large extent.* If the rate of evaporation is sufficiently great practically all of the sulfur is at first precipitated in this condition. The globules at first formed serve as centers of deposition for the balance of the sulfur separating from solution and under proper conditions grow to quite large dimensions. (Fig. 1.) The rubber, being a highly viscous mass, does not permit rapid migration of the sulfur and crystal formation is therefore somewhat retarded. After a short time crystallization usually takes place in two

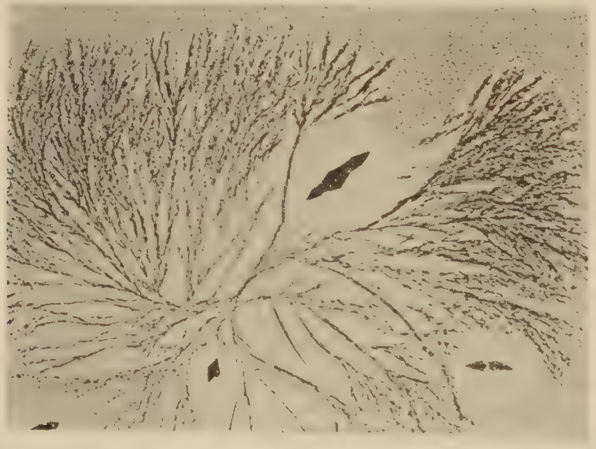

Fig. 3.—Dendrite winding its way through globules and rhombic sulfur crystals.

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* The protective action of the rubber is a powerful factor here. J. A.

forms; the ordinary rhombic and a branching dendritic made up of minute crystals. (Fig. 2.) The rate of evaporation of the benzol, and consequently the rate of separation of the sulfur from solution, is greatly decreased after most of the solvent has evaporated. The rate of sulfur separation then does not exceed the rate of crystallization and minute rhombic crystals are formed directly from solution. These crystals then serve as centers of crystallization and grow at the expense of the globules by a process of solution, diffusion and deposition. The globular form, being the less stable phase and therefore the more soluble, keeps the rubber supersaturated with respect to the crystalline phase which is then deposited. A gradual change of the less to the more stable form thus takes place through the medium of the solvent (rubber) until a considerable region around the growing crystals has been freed from

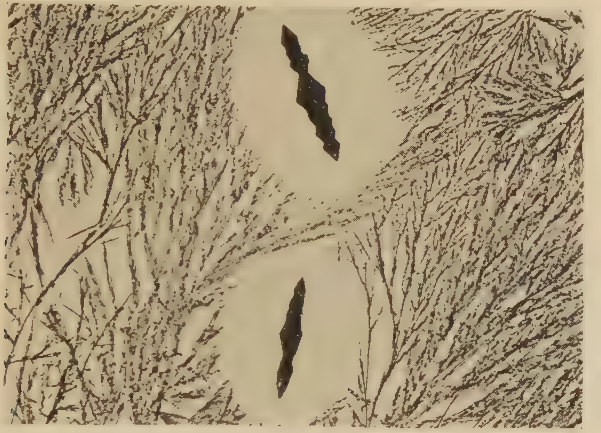

FIG. 4.—A later stage showing globules completely transformed into rhombic crystals and dendrites.

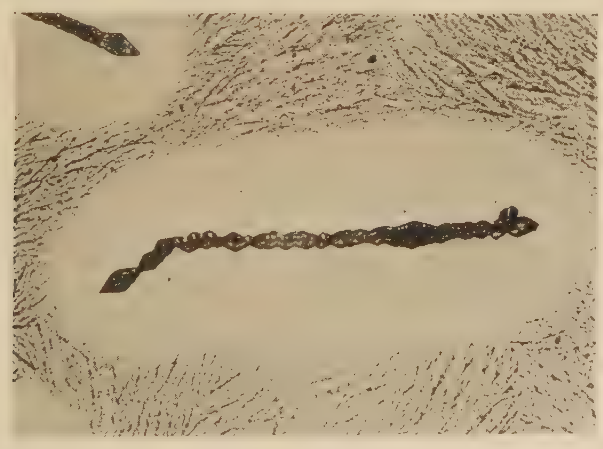

FIG. 5.—Rhombic crystals growing at the expense of the unstable dendritic form.

globulitic sulfur. As the rhombic crystals grow the distances between them and the globules become greater and their growth becomes slower as the sulfur must diffuse further. The remaining globules then go to form the more rapidly growing dendritic structure, the result being a mass of dendritic crystals with rhombic crystals here and there in the centers of clear areas containing no crystalline sulfur. (Figs. 3 and 4.) The dendritic arrangement winds its way through the mass of sulfur globules, from which it is always formed, branching out in all directions. This form is unstable and further growth of the rhombic crystals then takes place by means of its solution in the rubber and deposition upon the rhombic crystals present (Fig. 5), until ultimately all the undissolved sulfur is present in the form of rhombic crystals. Frequently impressions are left in the rubber where the dendrites have dissolved. In the absence of rhombic crystals to serve as crystal centers the dendrites themselves, by rearrangement, go over to well defined rhombic crystals. This process, however, proceeds very slowly, requiring several weeks for its completion at room temperature. On the other hand, in the presence of sufficient centers of rhombic crystallization no globules or dendrites will be formed on evaporation of the benzol, the sulfur separating from solution depositing directly on these crystals without passing through the intermediate forms. This can be accomplished by seeding with flowers of sulfur during the early stages before the sulfur has started to separate from solution. The crystalline form of the dendritic arrangement has not been determined, but it is very likely a variety of monoclinic sulfur formed from super-cooled sulfur just as the ordinary monoclinic variety is formed from molten sulfur.

Crystallization of Sulfur in Rubber

The solubility of sulfur in rubber is about 1 per cent at 20° C., 6.5 per cent at 95° and increases to more than 10 per cent at 110°. By heating any of the evaporated cement films from the above experiments for a few minutes at 110° the sulfur will completely dissolve in the rubber. Small globules of sulfur again appear on cooling and these then rapidly go over into the dendritic structure of minute crystals. Due to the uniform distribution of the sulfur in the rubber, the high viscosity of the latter and the rapid decrease in solubility on cooling, conditions are not favorable for the formation of the more slowly forming rhombic crystals at the outset. The dendrites, however, eventually go over to well defined rhombic crystals by rearrangement as described above. Even in the presence of rhombic crystal centers the rapid cooling of a heated specimen will cause the sulfur separating from solution to largely assume the globular condition followed by the transformation to the dendritic for the most part, for of the two crystalline forms under consideration the rhombic is the slower forming. The inversion from the less to the more stable form of a crystalline substance appears to be slower the more viscous the solvent. If, however, the specimen is cooled very slowly the rate of sulfur separation is then such that rhombic crystals can form directly from solution without first going through the globulitic and dendritic stages.

When rubber super-saturated with sulfur is seeded by innoculating or sprinkling with the solid phase crystallization results at the surface. If the specimen is touched with a relatively cold object while the free sulfur, or a part of it, is in the globular condition, the globules so disturbed crystallize at once. The larger part of this crystallization takes place at the surface as the globules there are most affected. The crystals at the surface then grow at the expense of the neighboring globules and after a short time a dense surface deposit of rhombic sulfur crystals is formed. (Fig. 6.) The solidified globules serve as crystallization centers and their formation is analogous to seeding with solid sulfur. Some dendrites are often formed at the same time, which later go over into regular rhombic form. Seeding with insoluble sulfur ($S\mu$) usually results in the formation of rosettes of needle-like crystals radiating out from the points of contact, while seeding with rhombic sulfur always produces regular rhombic crystallization.

Thus the presence of a viscous or plastic substance can influence and alter the normal crystallization and behavior of a crystallizing substance and bring about changes which are not ordinarily encountered.

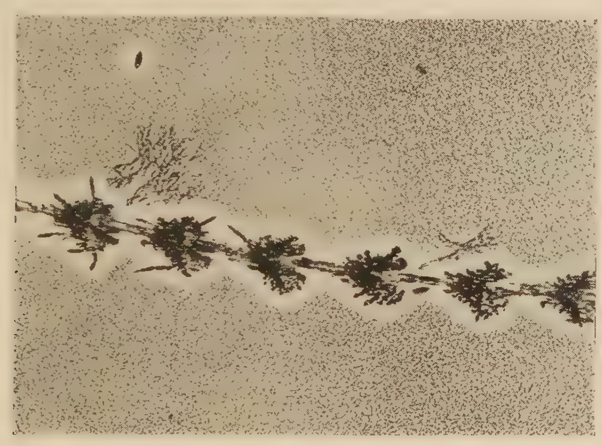

Fig. 6.—Solidified globules growing at the expense of still liquid globules. Crystallization induced by touching.

These experiments give some insight as to what occurs in metals, where increase in temperature and mechanical shock may speed up changes that would not register themselves within measurable time. In addition to crystal growth by dissolved sulfur crystallizing out on the growing crystals, the ultramicroscopic examination of sulfur separating from carbon disulfide in the presence of Canada balsam (J. Alexander, loc. cit.) indicates that there may be a preliminary grouping of the globulitic groups into what petrographers call *margarites* (a curved line of globulites looking like a string of pearls), or else into more or less symmetrical clusters. These must have undergone a very sudden readjustment to form larger crystals in Alexander's experiments, for only a few seconds elapsed before the solvent evaporated.

(Readjustments occurring during ageing, storage, etc., naturally also suggest themselves, *e.g.*, the occasional clouding of transparent toilet soaps due to the formation of crystals which may grow to quite large size.—J. A.)

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Ultramicroscopy

By Dr. Max Poser,
Bausch & Lomb Optical Co., Rochester, N. Y.

The illumination of very small particles contained in air, liquids, or solids with light of high specific intensity, at grazing incidence, will reveal objects of such small dimensions which we cannot render visible even with the highest power microscope equipped with objectives of largest numerical aperture obtainable.

To investigate this phenomena is essential, in order to enable one to differentiate as to the nature of these findings compared with those obtained with the regular microscope fitted with transmitted light arrangement and microscope objectives of greatest resolving power, to make comparison with the best results obtained with the so-called dark field illuminator.

Very small particles such as colloids in solutions, viscous substances, or in solids, that is, particles less in size than half the wave lengths of the light employed for illumination, will act like very small light sources when illuminated with an intense light of grazing incidence; and since the particles appear as small points of light irrespective of their shape or form, they present, so to speak, diffraction discs, each disc many times larger than the actual particle itself which consequently, are seen or traced under the microscope.

From this we learn that the particles themselves are not defined in their true shape or form by the optical system of the microscope and we therefore call such particles ultramicroscopic. Ultramicroscopic particles are therefore not objects resolved in their detailed structure like minute living cells, very small parasites or bacteria, etc., when viewed with the microscope with dark field illumination, but merely objects rendered traceable by means of their diffraction discs.

The method of illumination, specific intensity of light, wave lengths of light, numerical aperture of the microscope objective employed, as well as the magnification of the compound microscope, determine the smallest particles to be rendered visible by this method.

It is a well-known fact that with light of greatest specific intensity like our sunlight, we are able to render smaller particles visible than it is possible with the light of a carbon arc lamp.

Still weaker sources of light will not enable us to trace ultramicroscopic particles like colloidal gold, etc., less in size than 6 μμ. When investigating such extremely small particles, it is essential to illuminate not more of the depths of strata containing such particles than the objective on the microscope is able to depict; for which reason a precision slit adjustable in width as well as in length is essential.

The condensing system used for illuminating such a slit must be aplanatic and of a superior correction, in order to project the actual image of the source of light into the aperture of the slit. The aperture of the slit illuminated in this manner is then to be projected on a reduced scale into the object plane by means of a superior corrected lens system.

If the colloidal particles are suspended in a solution, the fluid chamber should have two optically plane surfaces at right angles to each other, and if the colloids are in solids, such solids must be prepared so that two optically plane surfaces at right angles to each other are available for the correct illumination and observation of the particles.

As a suitable microscope objective, a water immersion lens of about 4 mm. focal length with 0.6-0.7 numerical aperture and comparatively long working distance is advisable, in order greatly to facilitate matters. Care should be taken that the optical axis of the illuminating rays and the optical axis of microscope are carefully adjusted so that the axis of illuminating rays is perpendicular to the axis of the microscope.

An outfit of this description was used by Siedentopf and Zsigmondy in their studies of colloidal gold in ruby glass, etc., which demands illumination with light of great specific intensity and grazing incidence.

Light of great specific intensity, irrespective of volume, will render correspondingly smaller ultra-microscopic particles visible, since under such conditions the diffraction discs will appear larger than with light sources of lesser specific intensity.

According to Rayleigh, the intensity of the diffracted light diminishes as the square of the volume of the ultramicroscopic particle.

The above facts disclose to us that ultramicroscopic particles, as observed with the instrument described, are merely diffraction effects, since the particles themselves are too small to be resolved in detail. One might justly compare this phenomena with the stars in the sky seen at night.

Dark Field Illumination.

Stephens, the well-known English microscopist, constructed one of the first dark field illuminators, so-called reflex condenser, permitting an illuminating cone of light of 1.0-1.3 num. apert., which of necessity, represents an immersion dark field illuminator.

Dark field illumination can also be accomplished by a suitable central stop underneath the ordinary Abbé condenser, and the aperture of the microscope objective arranged so that no direct rays can enter the objective.

With these older forms of dark field illuminators, however, the illuminating beam is not well defined, and consequently diffused light is scattered over the object field, preventing well marked contrast of the delicate structures of the object with the background.

In later years dark field illuminators have been greatly improved, in order to furnish illuminating beams of superior correction so that the crossing point of illuminating rays is defined to a very small area with the margin of the light beam well marked.

The Kardioid condenser as devised by Siedentopf is of a high optical quality and forms an exact optical image of a small surface instead of a point in its conjugate focal plane; and since light proceeds invariably from surfaces and not from a point, the importance of this special correction is obvious.

With a dark field illuminator of this type, colloidal solution may be examined, but it is not suitable for colloids in solids.

Parallel rays entering a dark field illuminator of the ordinary type will also be brought to a focus, but the focal length varies from zone to zone and hence a luminous surface gives rise to innumerable image surfaces of different magnitudes, overlapping at the center.

Such a dark field illuminator would be inferior when used for investigation of colloids. On the other hand, it will prove superior when comparatively larger objects are to be examined as, for instance, living bacteria, granulation in leucocytes, etc.

Some dark field illuminators furnish very diffused illumination, which renders them suitable for comparatively large objects.

Many of the objects examined with the dark field illuminator of course could also be rendered visible in their bodily contour, delicate structures, etc., when stained and examined with the ordinary microscope of adequate resolving power; but since living objects, etc., cannot very well be stained for such observation, it is evident that the dark field illuminator forms a very useful accessory to the microscope.

A distinction, however, should be made between the average dark field illumination of unstained objects, like living bacteria, etc., and ultramicroscopic observation of colloids.

The first mentioned objects we can render visible in their shape and form. The latter only furnishes a method for tracing very minute objects by means of their diffraction discs and no bodily structure whatsoever could be determined by this method.

Dark field illuminators are usually fitted into the substage of the microscope in place of the Abbé substage condenser. The illumination usually employed is similar to that used for high-power microscopy, the light being reflected by means of the plane mirror of Abbé substage into the dark field illuminator and care should be taken that the dark field illuminator is precisely centered with the optical axis of the microscope.

The object is placed on a suitable object carrier and which in turn is connected with a drop of water or immersion oil to the upper surface of the dark field illuminator, in order to realize the full light beam, which should be from 1.00 to 1.40 num. apert.

The object is to be covered with a thin cover glass, which serves the purpose of totally reflecting the illuminating beam.

If a water immersion objective is used on the microscope, this, of course, should be connected by means of a drop of water with the upper surface of cover glass of object.

The numerical aperture of the objective employed should be less than 0.8 in order to insure a good dark background. To insure best results, the entire lens system, object slide and cover glass should be scrupulously clean.

Cotton and Mouton, "Les Ultramicroscopes et les Objects Ultramicroscopiques," and E. M. Chamot, "Chemical Microscopy" (J. Wiley & Sons, 1921), give a detailed description of the various types—Zeiss, Leitz, Jentzsch, etc. J. A.

The Immersion Ultramicroscope

By Prof. Dr. Richard Zsigmondy, Goettingen, Germany *

Ultramicroscopes used at present fall in two main classes: (1) those based on orthogonal illumination, and (2) those based on coaxial illumination. To the former group belong the original Siedentopf-Zsigmondy slit ultramicroscope, as well as the immersion ultramicroscope described below; to the latter group belong the numerous dark-field condensers used with the ordinary microscope, *i.e.*, the paraboloid and cardioid condensers of Siedentopf, the mirror condensers of Ignatowsky, Reichert, Jentzsch, etc.

The essential difference in the groups lies in the way the illuminating beam is directed and applied. In group 1 its axis is vertical to the optical axis, while in group 2 the illumination and optical axes coincide.

Hence arises a difference in applicability, the instruments of group 2 being especially well suited for the examination of bacteria and other microscopic objects, for light reactions, and at times for examining jellies; but they are not capable of bringing out very small sub-microns in colloidal solutions, because the superior illumination is overbalanced by inferiority in darkness of the field, which is affected by imperfections in the specimen and cover-glass.

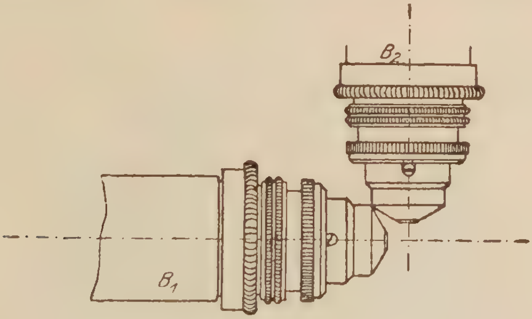

Fig. 1.

The disadvantage of the old slit ultramicroscope is that the illumination is inferior to that of some new condensers.

Since experience had taught me the advantages of side illumination and of being able to work with a cuvette or cell, and I saw that the new condensers offered no advantages for studying colloidal solutions, I set out to construct a new ultramicroscope, having the high-powered illumination of the first group. It is made by the R. Winkel Optical Works of Goettingen, and was first described in 1913,[1] since which time it has given highly satisfactory results both in my Institute and elsewhere, for it combines powerful illumination of the particles with an excellent dark field. The particles are about ten times as bright as with the old slit ultramicroscope. The instrument is based on the use of high-powered immersion objectives both for illumination and for observation, while careful construction of the instrument insures a perfectly dark field.[2]

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* Translated by Gertrude E. Alexander, B.L.

The wide aperture immersion objectives (Fig. 1, B_1 and B_2; Fig. 3) used for both illumination and observation are ground off on the side so as to permit the image of the source of light formed by the illuminating objective to be focused in the observation objective. (See Fig. 2.) A slit is not necessary, for an illuminating lens of short focal length, mounted on a rider, may be used to throw an image of the source of illumination into the image plane of the microscope objective, *B*. If a slit is used, it is best placed between the condenser and the illuminating lens.

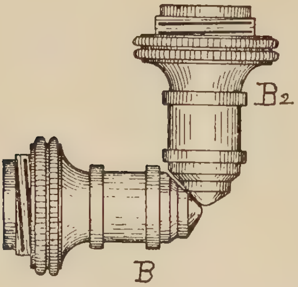

FIG. 2.

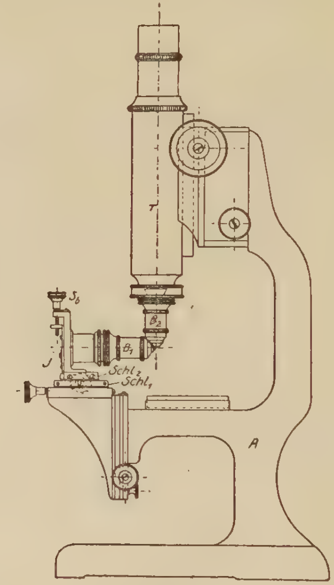

FIG. 3.

Figs. 4 and 5 show the light-cones of the original instruments. The narrowest constriction at *C* represents the image of the source of light or of the illuminated slit. In the meanwhile, Ehringhaus,[3] while maintaining the original principle, modified the instrument so as to make it more convenient, *e.g.,* in examining solids like glass.

Prior to the War, Mr. King of Glasgow determined the smallest particles of gold visible in Goettingen, using the brightest sunlight for illumination. The calculated size was about 4 μμ; but unfortunately the data of this gentleman were lost during the War. With an arc-light, particles of gold 8 μμ can readily be made visible and counted. The instrument has stood the test of time, and is preferable for the examination of colloidal solutions having tiny particles.

Among the new discoveries made with the immersion ultramicroscope is that by Thiessen and Baurmann,[4] of the thread-like structure of the vitreous humor of the eyes of mammals. It is interesting that the small amount of albumin in the vitreous humor is distributed in a network of ultramicroscopically fine threads, which, notwithstanding the trivial amount (one per thousand) gives it a jelly-like consistency. Ultramicroscopically, it can be determined that on gradual disappearance of firmness of the eye (fluidification of the vitreous humor), there can be observed a disintegration of the threads, a most striking fact being that the motion of the ultramicrons which develops on disintegration, is like that of pearls sliding along a thread or cord. Only the immersion ultramicroscope brings this out.

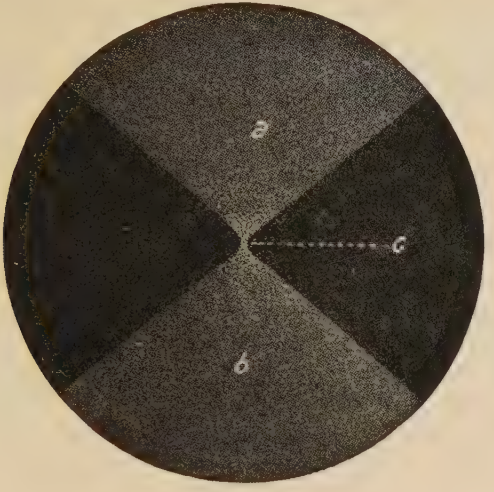

FIG. 4.

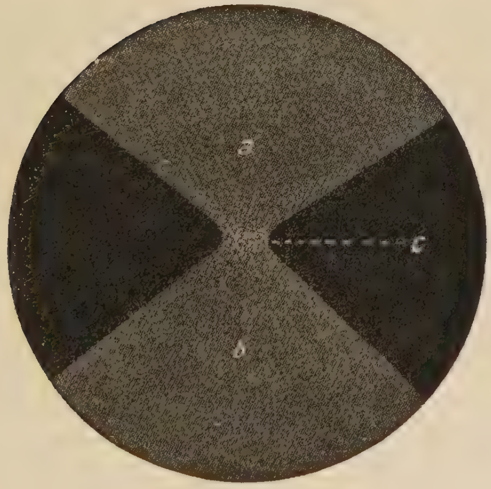

FIG. 5.

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Ultrafiltration and Electro-Ultrafiltration

By Prof. Dr. H. Bechhold,*
Director of the Institut für Kolloidforschung, Frankfurt a/M

One process of separating solid substances from fluids is filtration. For this purpose the pores of the filter must be finer than the diameter of the dispersed phase.† Since it has been shown that colloids are two-phase systems, it was obvious that it was possible to affect their separation by means of filters having pores of suitable fineness. Therefore, in order to separate dissolved colloids from their solvents and from dissolved crystalloids, use is made of jelly filters, which (after Bechhold) are called ultrafilters. They are used also in the separation of mixtures of colloids which have different sized particles.

HISTORICAL

The first experiments with the use of jelly filters were made by C. J. Martin,[1] who impregnated filter candles with gelatin and with silicic acid gel. He sought particularly to separate toxin-mixtures, which he filtered through such filter candles, using a pressure of 30-100 atmospheres. French experimenters (G. Malfitano, J. Duclaux, V. Henri, Borrel and Manea) used collodion sacs for the filtration of colloid solutions. Both methods, however, yielded such small amounts of filtrate and the filtration itself was so slow, that they did not prove practicable. The first really practicable method developed was the jelly filtration method of Bechhold [2] which he termed "ultrafiltration." This is described below.

Bechhold also demonstrated that the permeability (pore size) can be graduated by changing the concentration of the gelatin; the more dilute a jelly is, the more permeable it will be for a fine colloidal dispersion. He showed that colloids of different degrees of dispersity could thus be fractionated.

FILTER MATERIALS AND FILTER

In making jellies for ultrafilters, silicic acid gels and gelatin were used; although the latter was found practicable in many cases, more general use is made of solutions of nitro-cellulose in glacial acetic acid, in alcohol-ether, or similar solvents.

Sac or Thimble Filters.

For ultrafiltration, according to the procedure of the French experimenters, sac-like membranes of collodion can be used. Although these sacs at the present time are rarely used for real ultrafiltration, because they are inefficient and their applicability is very restricted, we will here describe the method of making them. They are very useful for experiments with animals, as they are easily inserted into body cavities.

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* Translated by Sylvia Josephi.

† Or else the filter pores may be reduced in size by the adsorption or deposit of a filter aid (*e.g.*, asbestos, kieselguhr) or by adsorption of something from the fluid being filtered.

To make collodion sacs, pour the collodion evenly over a round-bottomed glass cylinder, twirling continuously so that the excess drips off, until a thin, even coating is formed. Then plunge rapidly into water, so that the collodion jells. After most of the solvent (alcohol and ether) has been dissolved in the water (a process which takes minutes or hours, according to the thickness of the coating) the sac can be loosened from the underlying glass. To do this, cut a sharp ring around the periphery at the desired height, raise the edge carefully, keeping it constantly wet with water, much as one would skin an eel. For small ultrafilters test-tubes can be used instead of glass cylinders. By the use of larger cylinders sacs of 6 cm. in diameter and over can be made.

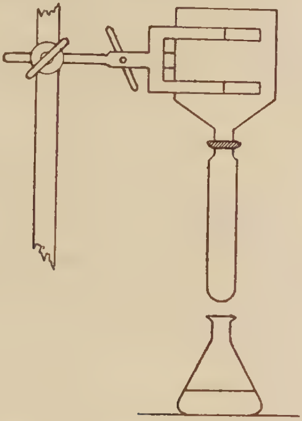

Fig. 1.

Instead of pouring the collodion on the outside, the same result can be obtained by pouring it inside the cylinder. The rest of the process is the same. In loosening the sac from the cylinder, in both cases, careful handling is required. The sacs must be continually moistened and kept moist. In employing these sacs for ultrafiltration the upper end is drawn over a ring of glass or wood, etc., fastened carefully with thread or silk and finally painted again with collodion. The ring is fastened to a stand and the sac is then ready for use.

Ultrafilter.

H. Bechhold uses for his ultrafilter flat layers of filter paper impregnated with a jelly. This paper foundation gives Bechhold's ultrafilter apparatus a strength that, under certain conditions, will withstand a pressure of 20 atmospheres or over. By this method it is also possible to make filters of any desired pore size.

For impregnation glacial acetic acid collodion * is most generally used. The solutions can be diluted with glacial acetic acid until the required concentration is obtained.

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* Solutions having a content of 10 per cent nitrated cotton and 2½ per cent potassium carbonate in glacial acetic acid, which solutions are characterized by slight contraction on gelatinization.

The dry sheets of filter paper are first steeped in acetic acid, then impregnated with glacial acetic acid collodion. Even mere dampening with water has yielded good results. It is important to note, however, that dry filter paper will not give workable results unless vacuum impregnation is resorted to.

The best filter papers are Nos. 566 and 575 made by Schleicher and Schüll of Düren, Rhineland. These are cut into sheets 9 cm. in diameter. If very exact scientific experiments are to be made impregnation in vacuum is advisable. Air is removed from the filters and the jelly forced into the filter paper by atmospheric pressure. The process is as follows:

The rectangular trough * *T* (see Fig. 2) has a cover *D* which is ground on air tight. A number of filter discs *F* are hung on the rod *S*. The cover *D* has two outlets. Through outlet *I* pass two tubes, one to the air-pump *L*, the other to the vacuum manometer *V*. When the air is exhausted from the trough, the jelly-producing fluid is admitted from the funnel *Tr*, which has a cock and a tube leading to the bottom of the trough. When the filters are covered the funnel cock is closed and the air cock opened, so that the gelatinous fluid is forced into the filters by atmospheric pressure. After a while (for low concentrations 10 to 20 minutes, for high concentrations 1 to 2 hours) the cover is removed and the rod with the filters is removed from the fluid.

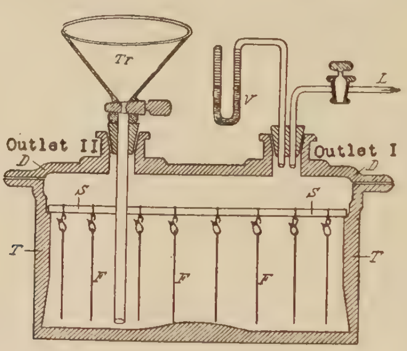

FIG. 2.

The same procedure is now followed irrespective of whether the filter discs have previously been wet with glacial acetic acid or water, or whether they have undergone vacuum impregnation. After the filter discs are removed from the glacial acetic acid collodion, each individual filter is allowed to drip while being constantly turned. Finally the whole filter is gelatinized suddenly by plunging it into an appropriate liquid. In the case of glacial acetic acid collodion water is used. If gelatin is being used, the entire impregnation trough must be placed in a warm water bath. The gelatin filters are hardened by plunging the wet filters after they have been allowed to gelatinize in the air, into chilled 2-4 per cent formaldehyd solution, and then allowing the whole to remain for some time in an ice-box.

The filters, irrespective of the way they have been made, are then washed for several days in running water and kept under water to which a little chloroform is added to prevent mould.

In 1918 Wolfgang Ostwald made the important observation that for many purposes usable ultrafilters can be made by pouring a double layer of collodion over a moistened filter paper, and after superficial drying, gelatinizing it with water.

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* This is made by Vereinigte Fabriken f. Laboratoriumsbedarf, Scharnhorststr., Berlin.

Ordinary smooth filter paper can be used as a substratum, which, as with other filters, is placed closely in a clean funnel; or else Schleicher and Schüll's filter thimbles are used. Wolfgang Ostwald's directions are to moisten the paper with *hot water* and allow it to drip. Then an ordinary but warm 4 per cent solution of collodion, say 20 to 30 c.c., is poured into the wet filter, and by quickly turning, the first or sizing layer of collodion is formed on the paper. The collodion should run but once over the paper and then be poured off. After this layer has dried 5-10 minutes, the stiffened filter is removed from the funnel, and again treated in like manner with collodion. After the collodion has once more dripped off, it is allowed to dry 5-10 minutes and is then plunged into distilled water, and in 20-30 minutes it is ready for use. The preliminary turbidity which appears on filtration is due to coagulated collodion.

By diluting the 4 per cent collodion with ether-alcohol (7 parts ether to 1 part alcohol) there are obtained filters of higher permeability and greater filtration speed.

Such ultrafilters can also be prepared on suction funnels, but a rubber gasket is necessary to make a tight joint between funnel and ultrafilter.*

If non-aqueous solutions (*e.g.*, benzol, alcohol, etc.) are to be ultrafiltered, the water in the filters can be eliminated by the successive application of solvents; for example, water can be replaced by means of acetone, and the acetone by benzol, etc.

Bechhold and Szidon[2a] suggested the more convenient method of using an appropriate organic solvent for coagulation. For the septa in question the most suitable solution was collodion in ether-alcohol, with benzene or toluene as coagulant. Ordinary ether-alcohol collodion is a 4 per cent solution, which may be diluted to vary pore-size of the filter.

Ultrafiltration Apparatus According to Bechhold.

The crying need of a simple arrangement for the purpose of ultrafiltration, led Bechhold to devise new apparatus suitable for laboratory practise. At his suggestion the Staatlichen Porzelanmanufaktur (Berlin) † produced various vessels (crucibles, dishes, suction funnels that can be cleaned, balloon filters, etc.) from a porous porcelain earth; they are not glazed on either side of the filter surface where the filtrate passes. (See Fig. 2a-2d.) They are coated on the filtering side with an ultrafiltering layer and then submitted to the suction of a water suction pump.‡

The application of the ultrafiltering layer is done similarly to the procedure with paper filters: The vessel is connected with the water suction pump, the crucible is attached to a glass "tulip" (as with a Gooch crucible), dishes are connected tight by means of a rubber gasket, etc., and they are then moistened with water filled with the impregnating solution (glacial acetic acid collodion, alcohol-ether collodion or the like). Suction is continued for 30 seconds, the solution is then shut off and the excess impregnating fluid is poured off with constant twisting, and that in the pores coagulated by quick plunging into water or into toluol if an ultrafilter for non-aqueous solutions is desired. If glacial acetic collodion has been used, the vessel is allowed to remain in the water until the acetic acid has diffused out, or it may be washed out on the suction tube with water, a few drops of ammonia or caustic soda being added at the end.

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* For details see Wolfgang Ostwald, "Kleines Praktikum der Kolloidchemie," Dresden, Theo. Steinkopff.

† To be had under the name "Ultrafilter apparatus," according to Bechhold-König Geräte from the Staatl. Porzelanmanufaktur, Wegelystr., Berlin, N.

‡ For further details see Bechhold and Gutlohn, "New Ultrafilter Apparatus," *Zeit. angew, Chem.*, 1924, No. 29.

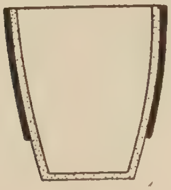

Fig. 2a.

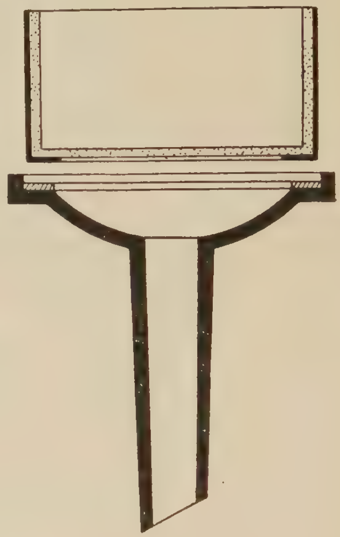

Fig. 2b.

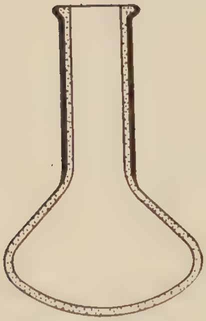

Fig. 2c.

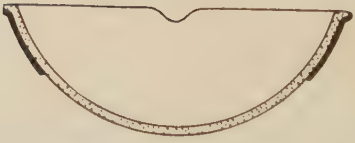

Fig. 2d.

Such a vessel like any other one of similar shape, is mounted on a suction flask and used with a water suction pump. Dishes and suction funnels hold large amounts of fluid; they may be stirred if needs be. By using balloon filters (similar in shape to Pukall filters) higher temperatures can be applied. For quantitative analysis the residue can be dried in the crucible and then ashed. The vessels may be cleaned by burning off or by soaking in chrome sulphuric acid.

It appears that with the aid of these vessels not only coarsely dispersed colloids, but even albumin, hemoglobin, and gelatin (glutin) may be concentrated by the water suction pump, and freed from crystalloids. Membranes for non-aqueous solvents may be formed on them and non-aqueous solutions ultrafiltered through them. In conclusion, it must be said that they are splendidly adapted to *electro-ultrafiltration*. Thus solutions of colloids containing electrolytes may be quickly freed from them (in 30 minutes), and concentrated.

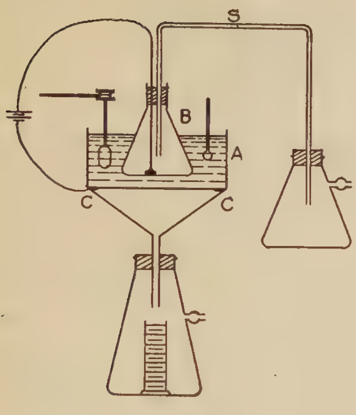

Fig. 3.

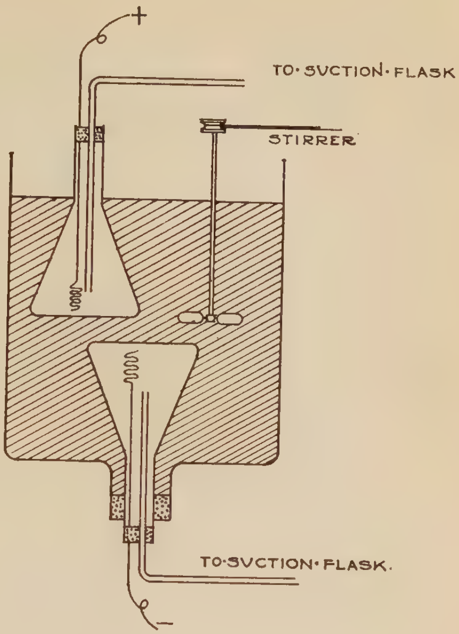

Fig. 4.

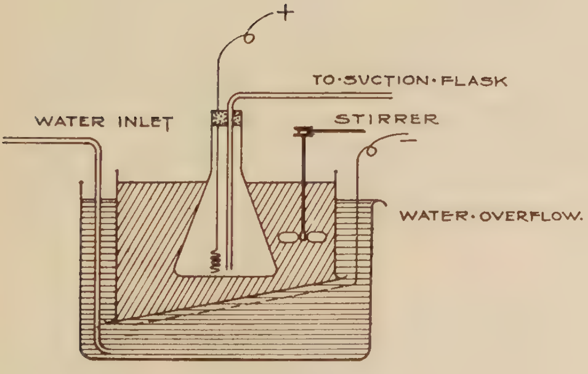

Fig. 5.

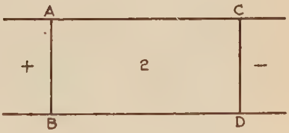

Fig. 6.

Membrane Filters.

This name is given to an ultrafilter offered by E. de Häen Chemische Fabrik "List" of Seelze bei Hannover; it is produced by the patented method of Zsigmondy and Bachmann. Like the Bechhold filters, they are flat discs; however they have no paper substratum, or base, but consist of the pure cellulose ester. They are made by pouring a solution of cellulose ester on glass plates. Whereas Bechhold varies the closeness of his filters by coagulating solutions of different concentration, this result is obtained in membrane filters by using mixed solvents, one constituent of which is more volatile than the other, and the evaporation is carried out in air having varied amounts of water. Prior to evaporation, a certain amount of water may be added to the cellulose ester solution, the amount varying with the pore closeness desired.

Since the various ultrafilters described above are the most useful, I refrain from describing unimportant variations. The filters may for the most part be used repeatedly, for precipitates are easily rinsed off. Bechhold's ultrafilters may, furthermore, be sterilized with steam under pressure, or in boiling water.

On the Use of and Results Obtained by Ultrafiltration

The choice of the suitable ultrafilter is much more dependent upon *the object to be attained,* than is the case with ordinary filtration. To effect the separation of a coarse suspension colloid (as for instance Prussian blue or colloidal silver solution) from its solvents, or if it is desired to retain in quantitative analysis the finest turbidities, for instance, calcium sulphate, a coarse pored ultrafilter should be used, which in spite of its high permeability for water, will retain the suspensions or suspension-colloids in question. Sacs are not to be considered.

However, if organic colloids—as for instance egg white or starch-solutions are to be ultrafiltered, that is, to be freed from water or from crystalloids, only dense Bechhold ultrafilters can be used. The speed of an ultrafilter (filtration velocity), all other factors and conditions of pore size being equal, is *proportional to the filtration pressure.* There is a specific minimum pressure that must be employed with every filter in order to force the fluid through it; for a filter that is just able to retain albumin, this amounts to about 20 mm. of mercury. In the case of organic colloids, an additional pressure is necessary to overcome the specific swelling pressure of the colloid in question. In the case of an 8 per cent solution of albumin, this amounts to about 40 mm. of mercury. In order to filter off water from an 8 per cent albumin solution, a minimum pressure of about 60 mm. of mercury is needed. Thus it appears that such an albumin solution cannot be filtered in an ordinary funnel, in fact that pressure must be used to obtain satisfactory ultrafiltration.

I therefore differentiate between *low pressure ultrafiltration* up to 1 atmosphere, for which *open* apparatus (funnels, suction funnels) can be used, and *high pressure ultrafiltration* at 1 atmosphere pressure and over, for which closed filters must be used.

Apparatus.

(a) *Low Pressure Ultrafiltration.*—For Wo. Ostwald's spontaneous ultrafiltration a simple funnel is sufficient, but it works slowly. It is more convenient to employ such arrangements as can be attached to a water suction syphon. Best for the purpose it seems to me are the Bechhold *ultrafiltration accessories*, such as the crucibles, suction funnels, dishes, flasks, etc., used in ordinary filtration, after they have been covered with an ultrafiltration layer.

For disc-shaped Bechhold ultrafilters and Membrane filters, which are to be used in connection with the water suction syphon, Zsigmondy recommends a sort of Büchner funnel, in which the cylinder shaped rim *B* (see Figs. 7 and 8) can be removed from the sieve plate *A*, and this again in its turn from the funnel *C*. This apparatus is made of porcelain (Fig. 7), also of metal (Fig. 8) and can be obtained from de Haen of Seelze, near Hannover.

The funnel *C* is mounted on a suction bottle, and upon this, connected by an air-tight rubber gasket, is set the porcelain or metal filter plate. This plate is covered by a sheet of ordinary filter paper and the ultrafilter placed upon it. Upon this is put another rubber gasket upon which the cylinder *B* is forced, in order to receive the fluid. Then the whole is held together by hand screws.

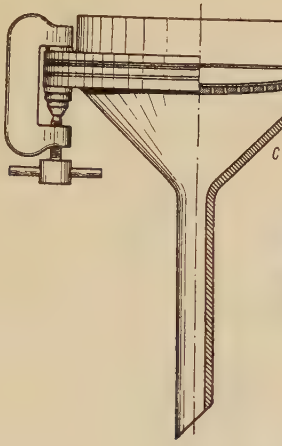

FIG. 7.

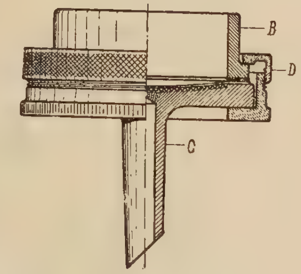

FIG. 8.

(b) *High Pressure Ultrafiltration.*—Bechhold has constructed an apparatus for high pressure ultrafiltration that can also be used for low pressure ultrafiltration. This is shown in Figs. 9-11.*

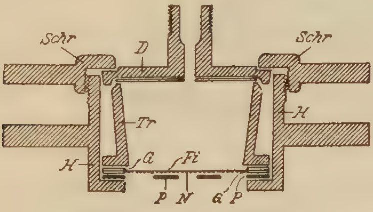

FIG. 9.

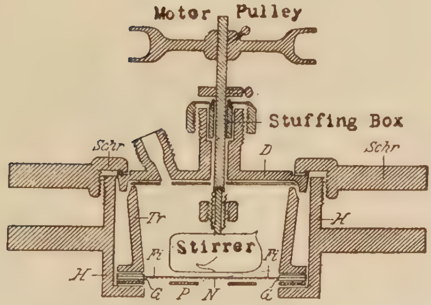

FIG. 10.

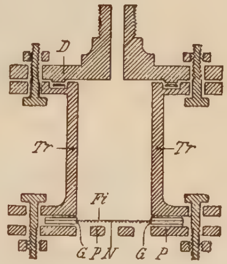

FIG. 11.

Figs. 9 and 10 are for medium pressure. Fig. 11 for very high pressure. The apparatus (Fig. 9) consists of a cylinder-like vessel *H*, upon which fits the actual filter *Tr*. Between the lower flanges *Tr* and *H* the round filtration discs *Fi* are pressed. The connection is made tight by the rubber gaskets *GG*. To avoid tearing the filter, it is placed on a nickel wire net or on a finely perforated nickel plate *N* and further protected against too much bulging by the coarsely perforated plate *P*. The funnel *Tr* is cone shaped above and is closed by means of the cover *D* ground to a conical fit and having rubber gaskets.

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* The apparatus is to be had from Ver. Fab. für Laboratoriumsbedarf, Scharnhorststr., Berlin.

By screwing down the closure *Schr*, both the cover above as well as the filter below are made tight in one operation. In the top of the cover is a small outlet with threaded connection for connecting up the pipe to the source of pressure.

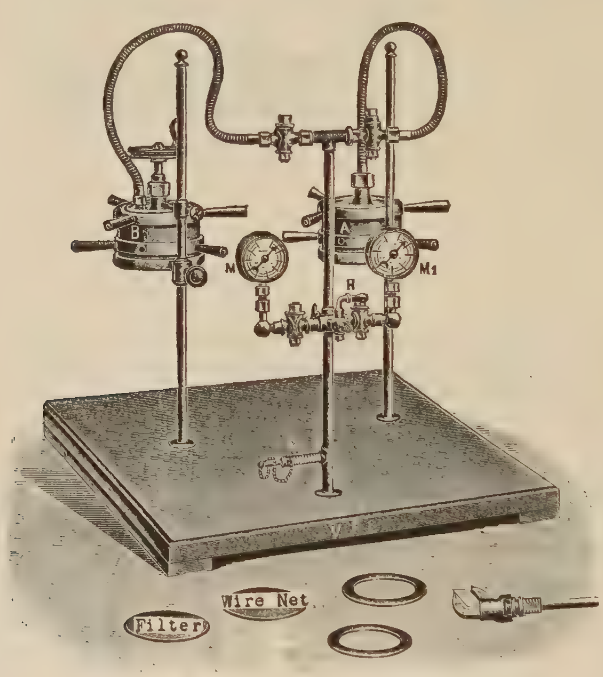

FIG. 12

Fig. 11, used especially for pressures above 10 atm., has a flange closure. This is naturally more cumbersome. Since in Fig. 11 the corresponding lettering specification is used, as in Fig. 9, a particular description is superfluous. Fig. 10 shows the apparatus with a stirrer, which in most cases is preferable, as the stirrer accelerates the filtration and the filtrate is of more uniform composition. In the absence of such stirring device, gel layers are apt to settle on the ultrafilter and act themselves as ultrafilters. In addition the apparatus must be carefully set up, and all openings, especially the stuffing box, must be carefully made tight against high pressure.

Pressure.—Pressure can be produced by means of a manually operated air pump. This method is specially adapted to scientific experimentation on behavior of filters; in short, where the measurements of very fine gradations of pressure are involved and when no long period of pressure is required. In cases of practical ultrafiltration a steel cylinder containing compressed air, compressed nitrogen, carbon dioxide, etc., is preferable.

Between the steel cylinder and the ultrafiltration apparatus a reducing pressure valve and two manometer *M* should be inserted, the very high pressure one to indicate the pressure in the steel cylinder, the other, behind the reducing valve, to register the low pressure on the ultrafiltration apparatus. By means of still another reducing pressure valve, together with its corresponding manometer, such fine differences in pressure may be produced that in my opinion such an arrangement can be safely recommended in place of the hand air pump for scientific measurements.

Fig. 12, which shows the complete equipment of the apparatus, further indicates another cock *H*, which may be used to cut off the pressure suddenly if necessary and so interrupt the process of ultrafiltration.

For high pressure ultrafiltration, several modified forms of apparatus have been developed. They showed no distinct advantages.

Gauging Ultrafilters.

It is generally necessary to be able to gauge the capacity of ultrafilters in order to ascertain the coarseness or fineness of its pores. Having done this, conclusions as to the particle sizes of the colloids under examination may be drawn.

A. *Gauging with Standard Solutions.*—For this purpose we may use solutions of coarsely dispersed → Night Blue or Prussian blue, Congo-red, collargol and 1 per cent hemoglobin ← finely dispersed. Even the coarsest pored spontaneous ultrafilters will retain Night Blue or Prussian blue, but hemoglobin demands tighter filters. Congo-red and collargol having particles about 40 μμ in diameter in the indicated order, are intermediate in the series above mentioned.

Ostwald's 2 per cent spontaneous ultrafilters generally retain Night Blue; the 4 per cent filters also hold back collargol.

Bechhold, Schleicher and Schull's 2 per cent ultrafilters retain Prussian blue; 5 per cent filters are tight against hemoglobin. The fact must be emphasized that the tightness of an ultrafilter is dependent not only upon kind and concentration of the impregnating solution, but also upon the kind and pore size of its foundation substance. Thus, ultrafiltration vessels made with unglazed porcelain as a base, are generally more permeable than those made of filter paper. In order to make the former tight against hemoglobin, 7 per cent glacial acetic acid collodion solutions must be used.

Bechhold has made the following tabulation for the permeability of ultrafilters. It is arranged in decreasing order of particle size of the colloids in solution, as ascertained by ultrafiltration with ultrafilters of various pore-size.

Suspensions
Prussian blue.
Platinum sol (Bredig).
Colloidal iron oxide.
Casein (in milk).
Colloidal arsenic sulphide.
Collargol (colloidal silver, von Heyden, about 40 μμ).
Gold solution No. 0 (Zsigmondy).
1 per cent Gelatin solution.
1 per cent Hemoglobin solution (molecular weight about 16,000).
Serum albumin (molecular weight about 5,000-15,000).
Diphtheria toxin.
Protalbumoses.
Gold solution No. 4 (Zsigmondy).
Bismon (colloidal bismuth oxide, Paal).
Lysargin (colloidal silver, Paal).
Colloidal silicic acid.
Lysalbinic acid.
Deuteralbumoses A.
Deuteralbumoses B (molecular weight about 2,400).
Deuteralbumoses C.
Litmus.
Dextrin (molecular weight about 965).
Crystalloids

B. The De Haen membrane filters have numbers indicating the number of seconds required for water to pass through. For instance, the number 50 on a filter indicates that, with good vacuum, it takes 100 c.c. of water 50 seconds to pass through a circular filter surface 100 mm. in diameter.

C. For the *precise determination* of the pore-measurements of ultrafilters Bechhold has developed the following methods:

1. *Air pressure method.*[3]—This method permits us to find approximately the *absolute* values for the coarsest pores in an ultrafilter. The principle is as follows: In order to force air through a capillary thoroughly wet with water, a certain amount of pressure is required, which is dependent upon the interfacial tension between water and air, which is constant, and the radius of the capillary.

If D is the diameter of the capillary, p the pressure in atmospheres, and β the capillary constant, the following formula applies:

$$D = \frac{4\beta}{p 1.033 \times 10^4}.$$

Assuming $\beta = 7.7$ at 18°, we get

$$D = \frac{30.8}{p 1.033 \times 10^4}.$$

By use of this formula the smallest diameter of the pores may be calculated after determining the *maximum pressure* required to force air through the pores of the completely saturated filter.

The *practical experimental procedure* is as follows: turn the filtrating apparatus upside down and place a thin layer of water on the filter (a few millimeters deep) and then observe carefully. What is the lowest pressure that will cause air bubbles to escape?

The diagrammatic sketch, Fig. 13, shows the filter apparatus in normal position. T = funnel, F = ultrafilter, L = air inlet. Fig. 14 shows it in the position ready to receive the air pressure, a shallow layer of water covers the filter. This method gives surprisingly large values for the coarsest pores of filters.[*] The reason for this is, that in an ultrafilter, there are always a certain number of very wide pores which are of no importance insofar as concerns the average of the filtrate. But it may also be that the laws applicable to wide capillaries must be modified when we reach this order of size. Experiments on this subject would be welcome.

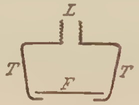

FIG. 13.

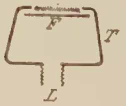

FIG. 14.

2. *Method based on the transpiration velocity of water.*—This method permits us to determine approximately correct values for the average diameter of the pores of ultrafilters. It is based on the somewhat indefinite formula of Poiseuille for the flow of liquids through capillary tubes.[4] Let D = diameter of pores, Q = quantity of water passing through the surface F, under constant

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[*] The figures given in the *Zeit. f. phys. Chem.*, 64, 328, *et seq.*, on the basis of this method are incorrect; they should be multiplied by 10.

pressure S. By R we represent the ratio of the vacant (water filled) space to the solid portion of the filter; it is calculated from the percentage content of solids in the jelly (a 5 per cent filter contains 5 per cent filled and 95 per cent vacant space). L is the length of the capillaries (which is not less than the thickness of the wet filter). k is a constant, dependent on the temperature and kind of fluid. Then the following formula applies:

$$D = \frac{Q(R+1)L}{k.S.F.R}.$$

If all experiments are conducted under the same conditions, $\frac{L}{k.S.F}$ becomes a constant and the formula is correspondingly simplified.

For a *practical experiment* two persons are required, one to regulate the pressure, the other to determine with a stop watch the amount of water passing in a definite time. Beneath the apparatus is placed a funnel, whose outlet may be closed by a rubber tube and a pinch-cock. The ultrafiltration apparatus is filled with water, pressure is applied until a definite pressure is reached. At that instant the pinch-cock beyond the funnel is shut so that all the water filtered at constant pressure is caught in the funnel. At the end of a definite time (1 minute) the pressure is instantaneously released. In this manner it is possible to measure how much water is forced through the filter in a given time. If, previously, the same experiment has been made, using filter paper of known pore size which is just able to retain, for example, blood corpuscles or bacteria which can be measured microscopically, it becomes possible by means of the above mentioned formula to calculate the average pore size of the ultrafilter.

This method shows that ultrafilters which are just able to retain hemoglobin have an average pore-diameter of 30-36 $\mu\mu$. (Probably this figure is too large.)

Ultrafiltration at Higher Temperatures.

For ultrafiltration at higher temperatures (for instance, glue, viscous oils, etc.), the funnel or the apparatus is placed in a wide tin or asbestos sleeve which is heated by a Bunsen burner (just like a hot water funnel). For high-temperature ultrafiltration, the balloon-shaped ultrafiltration apparatus (Bechhold-Koenig) is particularly convenient. The substance to be filtered is placed in a beaker or a boiler heated externally; the balloon filter, however, dips into the warm fluid.

Adsorption by Filters.

In ultrafiltration experiments care must be taken that adsorption does not cause trouble. It is therefore advisable to make a preliminary test of the solution to be handled, with a filter disc that has been cut into pieces, or by shaking it up with some of the powdered material constituting the apparatus, and then test it. If after shaking the content remains unchanged or nearly so, then no adsorption has taken place. With colored solutions very often the adsorption is indicated by a color change. If the ultrafiltration experiment has been invalidated by adsorption, it is advisable to use some other jelly for ultrafiltration. While, *e.g.*, arachnolysin is very powerfully adsorbed by glacial acetic acid collodion, it is very slightly adsorbed by formolgelatin.

In any event it is advisable, in ultrafiltration, to work quantitatively and to test both the filter residue and the filtrate for such changes as may be caused during the experiment.[5] It is essential that there be a *balance*.

A further source of error.—In experimenting with ultrafiltration of aqueous lecithin solutions, in the Institut für Kolloidforschung in Frankfurt a/M., Bechhold and Neuschloss[6] made an important observation. Lecithin forms a cloudy emulsion, in which the individual drops are several μ in diameter. When this was put through an ultrafilter which would retain hemoglobin completely, whose pores therefore <30 μμ in diameter, it came through cloudy when the pressure > 150g./cm.[2] The greater the pressure, the more turbid the filtrate. Bechhold[7] explains this as follows: the pressure deforms the lecithin droplets as they enter the capillaries so that they assume the smaller diameter of the capillaries, but upon their exit they again form drops of larger diameter. Therefore the diameter of the pores of the ultrafilter gives no definite idea of the diameter of a retained particle as far as *emulsions* are concerned, whose dispersed phase has a low surface tension against the dispersing phase.

Ultrafiltration Dialysis According to Wegelin.

Most of the arrangements for dialysis have the disadvantage, caused by the slowness of the process, of interchange between the solution contained within the dialyzing vessel and the external water. Therefore Wegelin[8] makes use of the properties of ultrafilters. He constructed an apparatus intermediate between a dialyzer and an ultrafiltration apparatus, especially designed for rapid dialysis; he called it a *percolator*, Fig. 15. It consists of a reversed funnel *a*, containing the colloidal solution which is to be purified; the funnel at the top is closed by an ultrafilter made tight by a rubber gasket. From the vessel *C* the washing fluid is forced through the funnel from the bottom upwards, and then flows off by means of the tube. By use of a pump it is possible to pump fresh wash fluid to *c* from the container *d* from time to time. This process is both practical and economical.

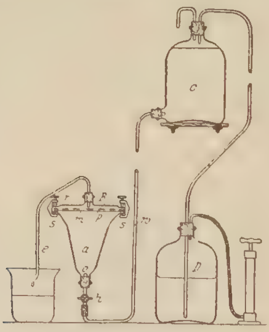

Fig. 15.

Applications of Ultrafiltration.

Ultrafiltration serves to separate colloids from crystalloids. It, therefore, can frequently take the place of *dialysis*. It is preferable to the latter on account of its more rapid working (the colloid is "washed") and because it accomplishes the separation without considerable dilution of the dialysate, which is unavoidable with the *dialyzer*. (See below, under Electro-Ultrafiltration.)

It was employed along this line in the separation of globulin and the electrolytes holding it in solution, of the products resulting from the digestion of casein by pancreatin (Bechhold), also of histidin in the hydrolysis of clotted blood.[9]

In quantitative analysis ultrafiltration has established a place for itself from the fact that it decidedly shortens many manipulations, thus saving much time.[10] By its use it was possible to simplify the investigation of silver salvarsan and similar compounds.[11] An especially important field of application of ultrafiltration exists in the fact that it permits us to separate colloids having different particle sizes (*fractional ultrafiltration*) or such substances about whose colloidal or crystalloidal nature doubt exists. In this connection attention must be called to the separation of various albumoses by Bechhold,[12] also further experiments by E. Zunz.[13] Studies concerning the nature of starch solutions by Fouard,[14] experiments for explaining cell-free fermentation processes by A. von Lebedew.[15] Grosser [16] ultrafiltered cows' and mothers' milk. He thus succeeded in differentiating simply between boiled and unboiled milk. By means of the ultrafiltration of urine Bechhold and Reiner [17] obtained the substances they called *stalagmones*. These consist of such semi-colloids as are found normally in urine (see Zandren [18]) which, however, through certain pathological processes, such as infectious diseases, nephritis, carcinoma, pregnancy, etc., are greatly increased (see Schemensky [19]) and which belong in the group of oxyprotein acids. They are evidently partly responsible for the increased time of sedimentation of blood corpuscles in serum (Fahraeus).

The ultrafilter has been found to be most useful in the study of toxins. Using this method Bechhold [20] proved that the toxon assumed to exist as an additional excretion of the diphtheria bacillus besides the toxin, is a much more strongly adsorbed poison and thus explains the chronic nature of the damage done by the toxon. Ultrafiltration was tried on various toxins (malignant edema, mallein, tuberculin, diphtheria toxin, tetanus toxin) by A. T. Glenny and G. S. Walpole.[21] For particulars the original must be consulted.

P. Kirschbaum [22] by this method demonstrated the acid nature of dysentery toxin, which is poisonous only when in the form of salts. Scheer [23] showed that the ultrafiltrate of milk of leutic mothers gives possitive Wassermann or Sachs-Georgi reactions.

Ultrafiltration is of especial importance for the study of equilibria in solutions, since by this method there is no change in the equilibrium between the crystalloidal and the colloidal ingredients. Naturally it must be understood that only small quantities should be filtered (so to speak, the differential established) in order that no changes in concentration occur. Upon this are based the numerous experiments on ferric oxid hydrosol by J. Duclaux and G. Malfitano.

Ultrafiltration has been variously employed for the solution of purely *biological* questions. For example, the experiments of Richter-Quittner,[24] who found that all substances exercising a swelling action (blood corpuscles in serum) increase the time required for ultrafiltration; those of von Burian [25] on the study of the function of the kidney glomeruli; those of Bechhold [26] on the problem of "internal antisepsis" and of pulsations in secretions; [27] recently for the explanation of kidney secretion, diuresis and edematous process (Ellinger [28]).

Ultrafiltration has acquired technical importance in the separation of drugs of therapeutic value from their impurities (resins, fats, etc.).[29] However, it has not yet found its proper place in industry.

Lastly, it must be stated that *fluids free from nuclei,* as well as *optically clear water* may be obtained by ultrafiltration: the latter is adapted for ultramicroscopic purposes (Bechhold [30]).

The question as to the applicability of the ultrafilter for the study of "filterable viruses" was discussed on the fifth day of the Freien Vereinigung für Micro-biologie (Dresden, 1911) by Doerr.

The electro-ultrafiltration process promises important results in freeing colloids from *electrolytes* (Bechhold).

A number of new experiments at the Institut für Kolloidforschung at Frankfurt a/M which deal with the ultrafiltration of glue may here be briefly referred to.

Recently Bechhold and Villa, by means of ultrafiltration have been able to render ultramicroscopically *visible, filtrable viruses and amicroscopic structures of indefinite* minuteness. They first eliminated coarse particles by filtration through a fine-pored porcelain candle, and then ultrafiltered out the more finely dispersed particles. The residual virus (or the like) was then gilded, fused into a microscope slide, and the gold "skeleton" developed as in photographic procedure. Molecular aggregates of albumin between 4 and 10 μμ of d'Herelle's bacteriophage, and what is probably the virus of smallpox, were thus made visible in the ultramicroscope.*

Electro-Ultrafiltration

As far back as 1903 Morse and Pierce [32] introduced a new method of purifying colloids. They passed a high tension direct current through gelatin enclosed in a parchment membrane immersed in pure water. Electrolytes migrated to the electrodes and were washed away by running water. This method, now called "electrodialysis," was widely employed by American investigators, and has also recently been studied by Wo. Pauli, Freundlich, and Farmer Loeb. What Ruppel and his collaborators and Prausnitz term the "electro-osmosis" method of purifying colloids, is essentially electrodialysis.†

It might be thought that electrodialysis simply hastens the elimination of electrolytes, at a rate varying with the intensity of the dialysis. A marked disadvantage of electrodialysis is *unbalanced neutrality* in the intermediate cell. Varying with the charge of the membrane, a current of water moves from one electrode to the other, most generally from the anode to the cathode, and this carries the products of the electrolysis into the intermediate cell. Furthermore, the Bethe-Toropoff phenomenon comes unpleasantly into evidence; this is an unbalanced neutrality in the membrane itself, whereby the *intermediate cell* acquires an alkaline reaction on the cathode side, and an acid reaction on the anode side. Various devices have been tried to circumvent this difficulty (using membranes of different charge, washing with certain salt solutions, etc.) without completely satisfactory results.

A material improvement of the method is *coupling ultrafiltration with electrodialysis,* which is readily done in the Bechhold-Koenig apparatus. Bechhold called this process *electro-ultrafiltration.* An electrode may be attached to the outer surface of an ultrafiltration crucible; a wire may be applied directly to the filtration side of the crucible, or we may use vessels painted lattice-fashion with metal, to which an electrode is attached.* The anode is immersed in the interior of the vessel (which is filled with the colloidal solution) and is furthermore separated from the solution by an ultrafiltration membrane which is formed on a balloon-shaped support. As the electrical transportation is taking place, suction is applied to both sides (ultrafiltration). (See Fig. 5.) The *products of electrolysis* are thus *sucked away,* and do not reach the interior vessel; thus the troublesome changes in reaction due to electrolysis are avoided or reduced to a minimum. Not only are electrolytes thereby removed, but also crystalloidal non-electrolytes. It is best to stir during the process.

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* See paper by d'Herelle, in Vol. II of this series. J. A.

† See paper by P. H. Prausnitz in Vol. III of this series, wherein are described the electro-osmosis methods of Graf Botha Schwerin. J. A.

This apparatus is *unusually flexible;* for small and even minute quantities an arrangement like Fig. 3 will do; for larger lots, one like Fig. 4. Here two balloon filters having ultrafiltration membranes, are placed bottom to bottom, the whole being enclosed in a large flask-shaped vessel—a salt-mouth minus its bottom will serve. For very large quantities there may be used an industrial type of dialyzer (Fig. 5), in which is immersed one or several balloon-shaped filters; the electrolyte drawn to the electrode within these filters, is sucked out. The other electrode lies below the dialyzer membrane, and any electrolyte appearing there is washed away by a stream of water. If the agitator passes through a germ-proof cover, the whole apparatus may be kept *sterile.*

There are several ways of maintaining the neutrality of the fluid under treatment.

We should see that the main course of the fluid is from anode towards cathode, so that there is a tendency to transport acid from the anode chamber into the fluid being treated. The anode should therefore be placed in the vessel having the greater acidity development. By bleeding off fluid just as soon as there is a difference in acidity, and also by choosing the correct size of suction vessel, the fluid may be kept neutral, acid or alkaline as desired. A further way of attaining a desired reaction, is to *reverse the current* at regular or irregular intervals.

The Electrodes.

Platinum or carbon are always used for anodes. For cathodes we may use carbon, iron, nickel, copper, or bronze. Wire mesh or spirals are convenient forms.

E. Heymann's [33] comparative calculations as to the efficiency of the various systems led to the following conclusions:

The dimensions of the apparatus should be essentially such that the two membranes (AB and CD, Fig. 3) should have an area of 33⅓ cm.^{2} as dialyzing or filtering surface. Distance between membranes, 3 cm. Volume of colloidal solution, 100 cc. Both electrodes should be directly behind the membranes, and should have an area equal to theirs; *i.e.,* 33⅓ cm.^{2} The membrane should be 0.1 cm. thick. No change in concentration should occur in chamber 2 (which is prevented by stirring). The initial solution should be $\frac{n}{7}$ with crystalloid, and be reduced to $\frac{n}{700,000}n$.

The following figures for the de-salting effect are reciprocals of the de-salting time. "De-salting" here means removal of "crystalloids."

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* These *Vessels for Electro-ultrafiltration* may be had of Staatl. Porzellanmanufaktur, Berlin, NW23.

DE-SALTING EFFECT.

Crystalloid Being Removed	NaCl	Cane Sugar
Dialysis	1	0.3
Ultrafiltration (hydrophobe colloid)	14	14.
" (hydrophile colloid)	4	4.
Electrodialysis (P.D. = 40 V/cm.)	168	0.3
" (P.D. = 10 V/cm.)	42	0.3
Electro-ultrafiltration (P.D. = 40 V/cm.)	172–182	4–14
" (P.D. = 10 V/cm.)	46–56	4–14
Ordinary electro-osmosis (P.D. = 40 V/cm.)	Ca 1	Ca 1

No definite calculation could be made as to the removal of crystalloids by a current of water on electro-osmotic transport of water, for this depends on the membrane charge; the figure 1 simply denotes a maximum, and indicates that the effect is of the same order of magnitude as with dialysis.

The above table shows the *advantage of ultrafiltration* over dialysis. It further shows that with the aid of the electric current electrolytes may be rapidly removed. Electro-ultrafiltration is the most rapid method, removing not only electrolytes, but *also other* crystalloids (mixtures of electrolytes and non-electrolytes).

Experiment has not only confirmed the above calculations, but the advantages of the new method over dialysis were even more marked, for the maintenance of uniform concentration in all purely dialytic processes encounters difficulties. Thus serum and glue solutions which take weeks to purify by dialysis, may be freed from electrolytes in 25 minutes;[34] the removal of other electrolytes occurs in correspondingly short time. Since certain proteins and other biocolloids are readily attacked by bacteria, molds, etc., speeding up the purification process (de-salting serum and other protein solutions) is of special significance. Avoidance of unbalancing the reaction, is another advantage of electro-ultrafiltration.

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Centrifugal and Diffusion Methods for the Study of Dispersity and Hydration in Sols

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For the frictional force f acting upon a spherical particle of radius r kept in motion with the velocity u in a dispersion medium of viscosity η we have the expression

$$f = 6\pi\eta r u \tag{1}$$

If the particle is not spherical, a determination of the frictional force, the viscosity of the dispersion medium and the velocity of the particle give us the radius of a particle frictionally equivalent to the particle studied. This quantity may, after Odén, be called the equivalent radius or simply the "radius" of a particle of unknown shape.

The problem is to formulate expressions for f and u which can be determined experimentally with a maximum of accuracy and a minimum of effort. It is further of importance that these expressions should permit not only the determination of the average size of particle, but also the distribution of sizes. All the experimental methods based upon equation 1 give the radius of the particle together with its adsorbed shell of dispersion medium, *i.e.*, these methods give the radius of the hydrated particle in the case where water is the dispersion medium. If by some other means we are able to determine the radius of the core of the system, these methods therefore offer a possibility of determining the thickness of the water-shell, *i.e.*, the degree of hydration of the particle. It will be shown in the following that the combination of centrifugal and diffusion methods enable us to draw some conclusions about the degree of hydration in cases where other methods have so far failed. It will also be seen that the combination of centrifuging and diffusion—either separate measurements on each of those phenomena or measurements on the combined phenomenon, viz.: the sedimentation equilibrium—make it possible to determine the real volume of the particle regardless of its shape, provided the density of the particle is known. This procedure may even be extended to the study of chemical compounds of very high molecular weight. If the partial specific volume at infinite dilution, *i.e.*, the volume change accompanying the addition of one gram of the substance to a large amount of solvent is known, the molecular weight may be found.

If the particle is exposed to the action of a centrifugal field the centrifugal force

$$4/3 \,.\, \pi r^3 (\rho_p - \rho_d)\omega^2 x$$

is equal and opposed to the frictional force

$$6\pi\eta r \,.\, \frac{dx}{dt}.$$

In this expression ρ_p is the density of the particle, ρ_d the density of the dispersion medium, ω the angular velocity, x the distance between the particle and the axis of rotation, and t the time.

Equating and integrating between the limits x_1 to x_2 and t_1 to t_2 we get [1]

$$r = \sqrt{9/2 \, . \, \frac{\eta ln(x_2/x_1)}{(\rho_p - \rho_d)\omega^2(t_2 - t_1)}} \tag{2}$$

In the case of a sol which only contains particles of one size, the quantity x_1 is the position of the boundary between sol and supernatant liquid at the time t_1, and x_2 the position at the time t_2.

If the sol is very fine-grained so that prolonged centrifuging has to be used, the diffusion of the particles must be taken into account. The effect is a more or less pronounced blurring of the boundary. If the centrifuging is fast enough to permit a zone of clear liquid to be formed close to the meniscus of the sol, *i.e.*, if the reflexion of the particles against the meniscus can be neglected and if the boundary is far enough from the bottom of the cell so that reflexion of particles from the bottom can also be neglected, the following simplified solution of the diffusion equation can be used to express the diffusion of the particles.[2]

$$c_z = c_o/2 \left(1 - \frac{2}{\pi} \int_o^y e^{-v^2} dy \right) \tag{3}$$

$$y = z\sqrt{\frac{3\pi N \eta r}{2RTt}} \tag{4}$$

where c_z is the concentration at the distance z from the sharp boundary which would have been formed if there had been no diffusion—z being positive in the direction towards the axis of rotation, c_o is the concentration of the sol at the time $t = o$, N the Avogadro constant, R the gas constant, T the absolute temperature. The function $\frac{2}{\pi}\int_o^y e^{-v^2} dy$ is the well known probability integral and can be computed from tables.[3]

The exact position of the boundary which would have been formed if no diffusion had taken place, can be determined by means of photographs of the rate of change of concentration with distance from meniscus. In case of $z = o$ we have $c_z = 1/2 \, . \, c_o$ and the position of the boundary is therefore the point where the concentration of the sol has fallen to half its value.

If the particle is hydrated, the thickness of the water layer can be found in the following way. Call the radius of the system: particle + water-shell R, the apparent radius determined from centrifuging r_a and assume that the density of the water-shell does not differ markedly from the density of the bulk of the water. Then we have [4]

$$4/3 \, . \, \pi r^3(\rho_p - \rho_d)\omega^2 x = 6\pi\eta R \, . \, dx/dt \text{ and}$$

$$4/3 \, . \, \pi r^3_a(\rho_p - \rho_d)\omega^2 x = 6\pi\eta r_a \, . \, dx/dt$$

thus

$$R = r^3/r^2_a \tag{5}$$

The macroscopic effect of centrifuging on a sol of equal-sized particles is not only a movement of the boundary but also a uniform decrease in concentration with time.[4] If the sol is contained in a sectorial cell with its center coinciding with the center of rotation and if c_t is the concentration after the lapse of the time t and c the original concentration we have,

$$c_t = c \, . \left(\frac{a}{x + a} \right)^2 \tag{6}$$

where a is the distance between the boundary of the particles at the start and x the same distance after the time t.

This equation can also be given the form

$$r = \sqrt{9/2 \, . \frac{\eta ln \sqrt{c/c_t}}{(\rho_p - \rho_d)\omega^2 t}} \tag{7}$$

which provides us with a new method of determining the size of particle from determinations of the decrease in concentration with time of centrifuging.

In virtue of their kinetic energy, the particles in a sol are kept in an incessant irregular motion—the Brownian movement—and a study of this motion gives us a means to determine the frictional force f. Instead of studying the movement of the individual particles, we can study the macroscopic result of the Brownian movements: the diffusion. For the diffusion constant D we have

$$D = \frac{RT}{Nf} \quad \text{or} \quad D = \frac{RT}{N \, . 6\pi\eta r} \tag{8}$$

The diffusion constant D is defined by the differential equation

$$dc/dt = D \, . d^2c/dx^2. \tag{9}$$

The general solution of this equation is too complicated to be used for experimental work. Under special conditions considerable simplifications can be introduced. In the case of colloid solutions where the diffusion is rather slow the most important simplification is the one already mentioned on p. 839. A column of dispersion medium is placed on top of a column of sol and measurements of the concentration as a function of the distance z from the original boundary are made before any appreciable amount of particles has reached the end of the layer of dispersion medium. This means that the two columns can be regarded as of unlimited length. The diffusion constant and the radius r of particle can be calculated from the equations (compare p. 839)

$$\begin{aligned} c_z &= c_o/2 \left(1 - \frac{2}{\pi} \int_0^y e^{-y^2} dy \right) \\ y &= \frac{z}{2\sqrt{Dt}} \\ D &= \frac{RT}{N \, . 6\pi\eta r} \\ y &= z \sqrt{\frac{3\pi N \eta r}{2RTt}} \end{aligned} \tag{10}$$

It was shown that in the expression for the frictional force obtained for the case that the particle is exposed to the action of a centrifugal field the density of the particle enters. In diffusion determinations, however, the density does not play any rôle at all. This fact makes it possible to calculate the density of the particle from centrifuging and diffusion experiments on the same sol. The elimination of r between the equations 2 and 8 gives

$$\rho_p = \frac{162\pi^2 N^2 \eta^3 D^2 ln(x_2/x_1)}{R^2 T^2 \omega^2 (t_2 - t_1)} + \rho_d \tag{11}$$

and between 2 and 4 gives

$$\rho_p = \frac{81\pi^2 N^2 \eta^3 z^4 ln(x_2/x_1)}{8R^2 T^2 \omega^2 (t_2 - t_1)^3 y^4} + \rho_d \tag{12}$$

It is hoped that these equations will permit us to determine the density of the particles in sols in cases where other methods have failed. If we have reason to believe that the particle of radius R consists of a core of radius r of material of known density ρ_m and a shell of dispersion medium, *e.g.*, water, the solvation—or hydration—of the particle can be found. Let ρ_a be the apparent density determined by equation 11 or 12, then we have for the thickness of the shell of dispersion medium

$$R - r = r\left(\sqrt[3]{\frac{\rho_m - \rho_d}{\rho_a - \rho_d}} - 1\right) \tag{13}$$

If the particle cannot be regarded as consisting of a core and a shell, but is built up of an amicroscopic structure of two phases, one of which is dispersion medium, the amount of the latter can be found. This method will probably be of importance for the determination of the hydration of proteins.

It is also possible to determine directly the frictional constant f from the diffusion measurements and introduce this value in the centrifuging equation. In this way we get a value of the volume v of the particle regardless of its shape. We have

$$f \,.\, dx/dt = v(\rho_p - \rho_d)\omega^2 x$$

$$f = \frac{RT}{ND}$$

thus

$$v = \frac{RT ln(x_2/x_1)}{ND(\rho_p - \rho_d)\omega^2 (t_2 - t_1)} \tag{14}$$

where x is increasing in the direction towards the center of rotation and c_1 and c_2 are the concentrations at the points x_1 and x_2 respectively.

If the particles are regarded as molecules of a definite chemical compound of molecular weight M, and partial specific volume at infinite dilution V, producing a solution of density ρ, we get

$$M = \frac{RT ln(x_2/x_1)}{D(1 - V\rho)\omega^2 (t_2 - t_1)} \tag{15}$$

The combination of centrifuging and diffusion data therefore provides us with a new method for the determination of molecular weights of substances with big molecules. Equation 15 does not involve any assumption regarding the shape of the molecule, the viscosity of the dispersion medium, etc. By means of centrifuging the value of $x_?/x_1$ corresponding to a certain time interval $t_2 - t_1$ and a certain angular velocity ω at a certain temperature T is determined. By means of diffusion experiments the value of the diffusion constant at the same temperature is measured. The quantities V and ρ can always be determined by pycnometric measurements.

Instead of measuring the centrifuging and the diffusion separately, one can combine them by measuring the sedimentation equilibrium. The variation of acceleration with distance from the center of rotation is taken into account by using the following differential equation [5]

$$dc/c = -N/RT \, . \, v(\rho_p - \rho_d)\omega^2 x dx$$

which integrated gives

$$lnc_2/c_1 = -N/RT \, . \, v(\rho_p - \rho_d)\omega^2 \, . \, (x_2 + x_1)/2 \, . \, (x_2 - x_1)$$

or

$$v = \frac{RTln(c_1/c_2)}{Nv(\rho_p - \rho_d)\omega^2 \, . \, (x_2 + x_1)/2 \, . \, (x_2 - x_1)} \tag{16}$$

If the particles are regarded as molecules we have

$$M = \frac{RTln(c_1/c_2)}{(1 - V\rho)\omega^2 \, . \, (x_2 + x_1)/2 \, . \, (x_2 - x_1)} \tag{17}$$

This important equation enables us to calculate the molecular weight from determinations of the concentration at the points x_1 and x_2 after sedimentation equilibrium has been reached. The temperature, the angular velocity of the centrifuge and the partial specific volume of the solute must also be known.

In the case of so-called colloid-electrolytes where the particle may be regarded as a polyvalent ion surrounded by a number of osmotically active ions of low valency (usually monovalent ions) or in the case where the particle has adsorbed a certain quantity of an electrolyte in such a way that a certain number of the ions of either sign are osmotically active the preceding equations for the velocity of fall, for the diffusion and for the sedimentation equilibrium require some modification.[6]

Suppose the colloid-electrolyte to consist of n-valent cations surrounded by n univalent anions. Let the molecular weight of the cations be M_c, of the anions M_a and the partial specific volume of the cations V_c and of the anions V_a. Further we call the mobility of the cations u and the mobility of the anions v and the concentration in mol per liter c.

By means of Nernst's method of reasoning [7] we derive the expression for the diffusion constant D in the following way. Call ds the mass of electrolyte which by virtue of diffusion passes a section 1 square centimeter of the diffusing column in the time dt, and call E the field potential caused by the partial separation of the cations and anions by diffusion, then we have:

$$\begin{aligned} ds &= -uc \, (1/c \, . \, RT \, . \, dc/dx + n \, . \, dE/dx)dt \\ nds &= -vnc \, (1/c \, . \, RT \, . \, dc/dx - dE/dx)dt \end{aligned}$$

thus

$$ds = -RT \, . \, \frac{uv(n+1)}{nu + v} \, . \, dc/dx \, . \, dt$$

which gives

$$D = RT \, . \, \frac{uv(n+1)}{nu + v} \tag{8a}$$

If we call the frictional coefficient for one mol of cations $F_c = 1/u$ and for one mol of anions $F_a = 1/v$ this equation can be given the form

$$D = \frac{RT}{\left(\frac{F_c + nF_a}{n+1}\right)} \tag{8b}$$

If the ions may be regarded as spherical with the radius r_c and r_a respectively, we get

$$F_c = N \, . \, 6\pi\eta r_c \quad \text{and} \quad F_a = N \, . \, 6\pi\eta r_a$$

thus

$$D = RT/N \, . \, \frac{1}{6\pi\eta\left(\frac{r_c + nr_a}{n+1}\right)} \tag{8c}$$

The velocity of fall of a colloid-electrolyte in a centrifugal field can be found in the following way.[8]

For the cations we have

$$\omega^2 x M_c(1 - V_c\rho) - n \, . \, dE/dx = 1/u \, . \, dx/dt$$

and for the anions

$$\omega^2 x M_a(1 - V_a\rho) + dE/dx = 1/v \, . \, dx/dt,$$

thus after elimination of E and integrating

$$M_c(1 - V_c\rho) + nM_a(1 - V_a\rho) = \frac{(nu + v) ln x_2/x_1}{uv\omega^2(t_2 - t_1)} \tag{15a}$$

By means of equation 8a the mobilities can be eliminated,

$$\frac{M_c(1 - V_c\rho) + nM_a(1 - V_a\rho)}{n+1} = \frac{RT ln x_2/x_1}{D\omega^2(t_2 - t_1)} \tag{15b}$$

The sedimentation equilibrium for a colloid-electrolyte can be found in the following way. When equilibrium is reached the mass ds of the electrolyte which streams through the section 1 square centimeter towards the center of rotation during the time dt by virtue of diffusion, must be equal to the mass streaming towards the periphery by virtue of the fall.

The fall of the cations gives

$$ds = uc[\omega^2 \times M_c(1 - V_c\rho) - n \, . \, dE/dx]dt$$

and the fall of the anions

$$ds = vc[\omega^2 \times M_a(1 - V_a\rho) + dE/dx]dt$$

thus

$$ds = \frac{uv\omega^2 \times c[M_c(1 - V_c\rho) + nM_a(1 - V_a\rho)]}{nu + v} \, . \, dt$$

On the other hand we have just shown that for the diffusion

$$ds = -RT \, . \, \frac{uv(n + v)}{nu + v} \, . \, dc/dx \, . \, dt.$$

Equating and integrating we get

$$\frac{M_c(1-V_c\rho)+nM_a(1-V_a\rho)}{n+1}=\frac{RTlnc_1/c_2}{\omega^2\left(\frac{x_2+x_1}{2}\right).(x_2-x_1)} \tag{17a}$$

The last equation is of especial interest. If M_a is small compared with M_c and n a comparatively great number we have the approximate equation

$$M_c=\frac{nRTlnc_1/c_2}{\omega^2(1-V_c\rho)(x_2+x_1)/2.(x_2-x_1)} \tag{17b}$$

By means of this equation it is possible to calculate the molecular weight of the slow ion of a colloid-electrolyte if the number of osmotically active ions of opposite sign is known.

The distribution of size of particle in a sol can be found from centrifuging data in the following way, provided any notable diffusion has not taken place during the time of centrifuging. In a thin layer dx of the sedimenting sol the change in concentration dc_t from the section at x to the section at $x+dx$ is due to particles with radius r to $r+dr$, the values of r being determined from equation 2. If dc_t/dx is measured the distribution function dc/dr is found from the expressions

$$dc/dr=dc/dx/dr/dx \tag{18}$$

$$dc=dc_t.\left(\frac{x+a}{a}\right)^2.$$

Thus we have

$$dc/dr=\frac{dc_t/dx}{dr/dx}.\left(\frac{x+a}{a}\right)^2 \tag{19}$$

In the case of very small particles the influence of diffusion upon the variation of concentration with distance from the axis of rotation has to be taken into account. If the sol is comparatively uniform, it is sufficient to determine the percentage mass of a few size-classes. The diffusion curves for these particles are calculated by means of the equations 3 and 4. For a certain time of centrifuging the position of the boundary lines which these particles would have given are calculated from equation 2. The position of these boundaries constitute the zero points for the different diffusion curves. These theoretical data enable us to calculate for different distances x from the meniscus of the sol the contribution $c_{I,x}$ which each size-class gives to the total concentration c_x. These contribution terms have to be multiplied by the factor $\left(\frac{a}{x+a}\right)^2$ and by the factor F_I which expresses the relation between the mass of each size-class and the total mass of the disperse phase. Thus we have

$$c_x=\sum_{I}^{k}F_I.c_{I,x}.\left(\frac{a}{x+a}\right)^2 \tag{20}$$

If k size-classes are chosen k observations are necessary to determine the unknown quantities F_I, F_{II}, . . . F_k. The system of equations obtained can be solved conveniently by means of determinants if the number of unknowns, that is, the number of size-classes chosen, is low. If the number of size-classes is high the method of successive approximation must be used.

From pure diffusion data the distribution of size of particle can be found by a method of calculation similar to the method just described. The particles in the sol are distributed into a number of size-classes $I, II, \ldots k$ and the contribution $c_{I,x}$ which each of these size-classes gives to the total concentration c_x in a point at the distance x from the original boundary between sol and pure dispersion medium is calculated from equations 3 and 4. The sum of all these contributions, each of them multiplied by the factor F_I which expresses the relation between the mass of each size-class and the total mass of the dispersed phase, give the value of c, or

$$c_x = \sum_{I}^{k} F_I \cdot c_{I,x} \qquad (21)$$

The values of $F_I, F_{II}, \ldots F_k$ have to be found from a system of equations in the same way as we have already described it on p. 843.

From measurements of the sedimentation equilibrium the distribution of size of particles can be found in an analogous way. We get

$$c_x = \sum_{I}^{k} c_I \cdot e^{-Av_I x^2} \qquad (22)$$

$$c_I \int_{0}^{h} b_x e^{-Av_I x^2}\, dx = F_I \qquad (23)$$

where $A = N/2RT \cdot (\rho_p - \rho_d)\omega^2$, b_x is the width of arc of the column of sol at the point x, v_I is the volume of a particle of the first size-class, c_I the concentration of the first size-class at the bottom of the cell and h the height of the column. The bottom of the cell is taken as the origin of x and this quantity is taken positive in the direction towards the center of rotation. The total mass of the disperse phase is taken = 1 and the depth of the column of sol is taken = 1. As shown by Rinde the integral in equation 23 can be solved after introducing the expression for b_x against x and computing the area between zero and h. If this value of the integral is B then $c_I = F_I/B$ is substituted in equation 22 and this equation is then treated as equations 20 and 21.

The technique of measurement used so far for the realization of the experimental conditions of the preceding equations is briefly summarized on the following pages.

The experimental details of the centrifuging methods have been worked out by Nichols and the writer in the University of Wisconsin chemical laboratory[9] and by Rinde and the writer in the University of Upsala chemical laboratory.[10] The first instrument built allowed the determination of size of particle down to $r = 20\ \mu\mu$ in the case of gold. The second instrument—for which the name *ultracentrifuge* is proposed—has been used for the determination of gold particles down to $r = 2\ \mu\mu$ by the method of measuring the rate of fall of the particles. By means of measuring the sedimentation equilibrium it is now being used for the study of size of particle and molecular weight of proteins. Measures have also been taken in order to extend the range of the ultracentrifuge still further.

The construction of the ultracentrifuge is shown in Figs. 1, 2 and 3. The sol to be studied is enclosed in a special cell of sectorial shape having plane parallel windows. One of the types of cell used is shown in Fig. 3. It takes about 1 c.c. of sol. After filling the cell is closed by a small fiber stopper. The rotor 5 Fig. 1 which carries the cell rests on the vertical shaft 15 Fig. 1 and these two parts together form a "spinning top." The energy of rotation is delivered by the motor D Fig. 2 and transferred to the shaft 15 by an endless screw device and a system of special couplings which serve to isolate the rotor from the vibrations in the motor and the pulley C Fig. 2.

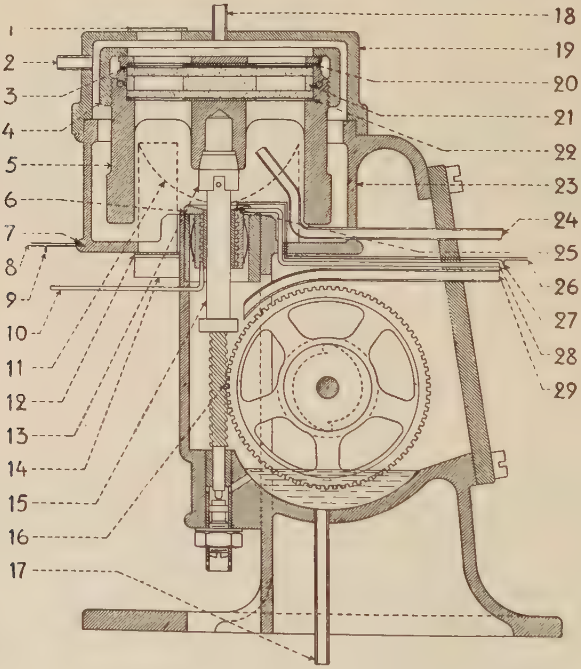

Fig. 1.—Diagram of the ultracentrifuge.

The speed of the rotor can be varied from 5,000 to 10,000 revolutions per minute. To prevent convection currents being formed in the sol, it is necessary to keep the sol at constant temperature during centrifuging. Hydrogen gas of constant temperature is therefore passed around the rotor (see 18, 24, 2 Fig. 1 and E, F Fig. 2), water is passed through a spiral slot in the bearing 6 Fig. 1 and oil of constant temperature kept in motion by a circulation pump G Fig. 2 is constantly poured on the endless screw 16, 29 Fig. 1. Thermocouples 25, 7 Fig. 1 in the bearing 6 and in the casing of the centrifuge enable the experimenter to control the temperature difference between bearing and casing. This difference should not exceed 0.3°.

To permit observations of the sol during centrifuging, the casing is provided with two windows 12, 1 Fig. 1, one in the bottom and one in the lid. Below the lower window a reflecting prism 14 Fig. 1 is mounted so as to direct a horizontal beam of light vertically through the centrifuge. A cir-

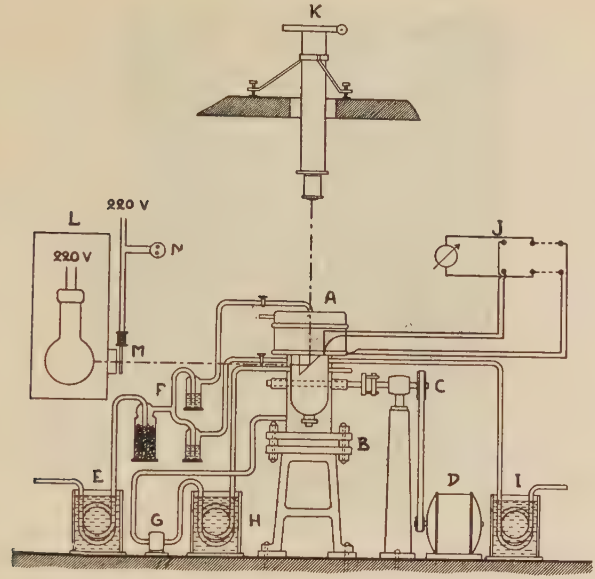

FIG. 2.—Diagram of experimental arrangement for ultracentrifuging.

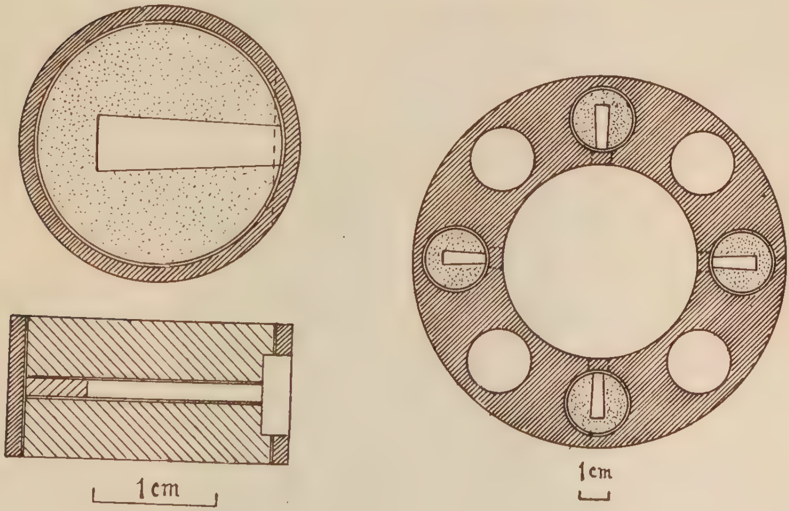

FIG. 3.—Cell for the ultracentrifuge.

cular disc of ebonite 3 Fig. 1 with an aperture coinciding with one of the sectorial cells is placed on top of the glass cell and cuts off all the light except the light which has passed the sol in the sector in question. The other sector serves only as counterweight. At some distance from the centrifuge a 500 watt Philip's Argenta lamp fed by storage cells is mounted providing an intense and even source of white light (L Fig. 2). A cell 5 cm. deep con-

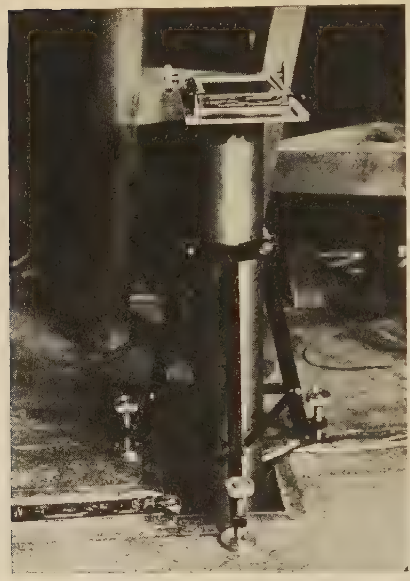

Fig. 4.—Camera for the ultracentrifuge.

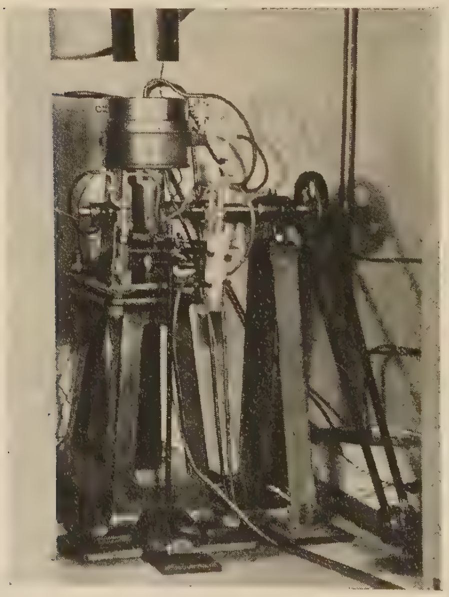

Fig. 5.—The ultracentrifuge.

taining water is inserted between lamp and reflecting prism to cut out the ultra red. Observations are made from a room above the one where the centrifuge is mounted, through an aperture in the ceiling. By means of a special camera K Fig. 2 and Fig. 4 provided with an objective of 55 cm. focal length, photographs of the sol are taken during centrifuging. The shutter M Fig. 2 is controlled by means of an electromagnet and can be operated from the room where the camera is mounted. The galvanometer for the thermocouples and the device for the control of the water current for the bearing 6 Fig. 1 are also placed in the upper room.

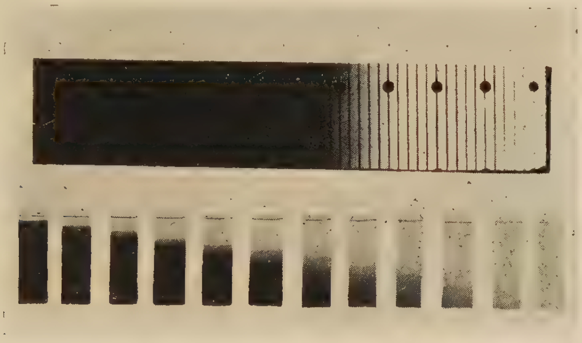

Fig. 6.—Photographs of the sedimentation of a gold sol of 11.6 μμ average radius during centrifuging at a speed of 5700 r.p.m.

For the study of certain proteins all glass parts of the apparatus through which the illuminating beam passes are replaced by quartz and a quartz mercury lamp is used for illumination.

When studying the sedimentation equilibrium, it is necessary to have the centrifuge running for a considerable time to ensure complete equilibrium. The instrument described above has been kept running for 70 hours at a speed of 10,000 r.p.m. without any disturbance occurring.

Fig. 5 gives a view of the centrifuge.

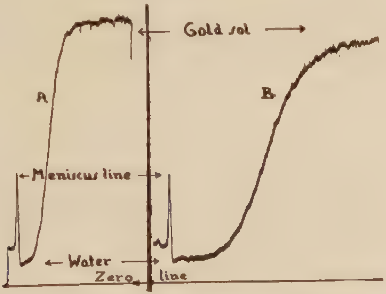

Fig. 7.—Microphotometric records of the sedimentation of a gold sol of 11.6 μμ radius.

As an example of the use of the ultracentrifuge a few data from the study of a gold sol of average radius 11.6 μμ are given. Twelve exposures of the sol in question were made during centrifuging (speed 5700 r p.m.) every 5 minutes. On the same plate was printed a neutral tint wedge (Fig. 6). On another plate a series of exposures of the same sol in different degrees of dilution were made shortly after starting the centrifuge; the same wedge was printed on the second plate. All the pictures of the sol as well as the prints of the wedge were then recorded by means of a self-registering Siegbahn microphotometer. In Fig. 7 two such records are reproduced, A representing the 2nd and B the 5th of the exposures in Fig. 6. By means of these microphotometric records the curves giving the relation between concentration of the sol and the distance from the meniscus, viz., from the axis of rotation, can be constructed, if necessary corrections for the variation of light-absorption with size of particle are introduced. In Fig. 8 these concentration curves for the sol in question are reproduced. The distribution curve calculated by means of one of these concentration curves is given in Fig. 9.

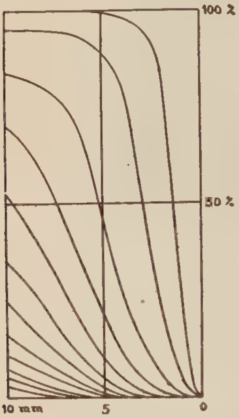

Fig. 8.—Diagram giving the relation between concentration and distance from center of rotation in a gold sol during centrifuging.

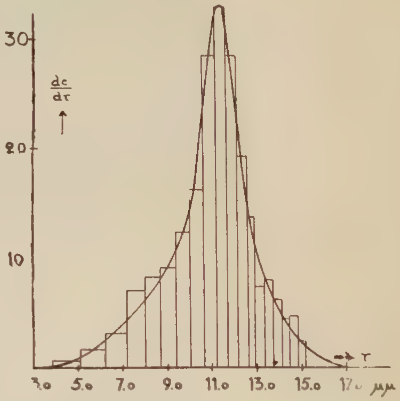

Fig. 9.—Distribution of size of particle in a gold sol determined by means of the ultracentrifuge.

To demonstrate the case where the influence of diffusion has to be taken into account some data from the study of a more fine-grained gold sol are given in Table 1.

TABLE I

Distribution of Size of Particle in a Gold Sol Calculated from a Photograph of the Sol During Centrifuging

$t = 7200$ sec.
$\omega = 190\ \pi$
$T = 289°$

Radius of Particle in μμ	Mass of Particles in Per Cent of Mass of Total Dispersed Phase
1.5	0.7
2.0	0.3
2.5	4.5
3.0	20.7
3.5	35.2
4.0	34.4
4.5	0.0
5.0	0.0

An example of the determination of size of particle in a very fine-grained gold sol prepared by reducing gold chloride with phosphorus is given in Table 2.

TABLE II

DETERMINATION OF SIZE OF PARTICLE IN A GOLD SOL BY MEANS OF THE ULTRACENTRIFUGE
Speed = 8700 r.p.m., $\omega = 290\ \pi$, $T = 290$.

Time of Centrifuging in Sec.	Distance between Axis of Rotation and Inflexion Point of Concentration Curve in Cm.	Concentration in Per Cent Original Sol.	Radius of Particle in $\mu\mu$ Calculated from: $r = \sqrt{\dfrac{9\ \eta\ ln\ x_2/x_1}{2(\rho_p - \rho_d)\omega^2(t_2 - t_1)}}$	$r = \sqrt{\dfrac{9\ \eta\ ln\ (c/c_t)}{2(\rho_p - \rho_d)\omega^2\ t}}$	Zsigmondy's Nuclear Method
3600.......	3.70	100	—	—	—
5400.......	3.78	—	2.0	—	—
7200.......	3.87	75	2.1	2.4	—
9000.......	3.96	68	2.1	2.6	—
9900.......	4.00	59	1.9	2.9	—
			Average 2.0	Average 2.6	2.5

As an example of the determination of molecular weights by means of the ultracentrifuge some data from a recent study on hæmoglobin carried out by Fåhraeus and the writer are given in Table III.

TABLE III.

DETERMINATION OF THE MOLECULAR WEIGHT OF CARBONMONOXIDE-HEMOGLOBIN BY MEASUREMENT OF THE SEDIMENTATION EQUILIBRIUM ON THE ULTRACENTRIFUGE.

Speed = 8700 r.p.m., $\omega = 290\ \pi$, $T = 293$, $t = 39$ hours, partial spec. volume = 0.749.

x_1	x_2	c_1	c_2	M
in cm.		in gr. per 100 cc.		
4.61	4.56	1.220	1.061	71300
4.56	4.51	1.061	0.930	67670
4.51	4.46	0.930	0.832	58330
4.46	4.41	0.832	0.732	67220
4.41	4.36	0.732	0.639	72950
4.36	4.31	0.639	0.564	60990
4.31	4.26	0.564	0.496	76570
4.26	4.21	0.496	0.437	69420
4.21	4.16	0.437	0.388	66400
			Average	67870

For the determination of diffusion constants according to the equations 3 and 10, the following experimental arrangement has been worked out by Janson and the writer and is now in use in the writer's laboratory. The diffusion cell is shown in Fig. 10. By means of the stop-cock A with double bore and three outlets, the solution can be run down very slowly from the vessel B into the diffusion vessel C which has been provided with a suitable quantity of solvent or dispersion medium. The cell is mounted in a special stand—not shown in the figures—which permits the stop-cock to be manœuvered from the outside of the thermostat holding the cell. It is isolated with regard to vibrations transmitted from the surroundings by means of a special arrangement similar to the Julius suspension [11] (Fig. 11). The stand A carrying the diffusion cell is suspended at three points situated in the plane through the center of gravity of the system and supported by three spiral springs B and thick rubber plates C, which rest on three iron pillars D. The counterweights F serve to adjust the center of gravity and bring it into the plane of the boundary between the diffusion solution and the solvent. This position means a minimum of vibrations in the diffusing liquid. The diffusion cell is surrounded by a thermostat G, containing either ice or water of the temperature wanted. The diffusing solution can be illuminated either from behind or from both sides by means of suitable lamps, and pictures of the diffusing column are taken from time to time. The camera used for this purpose has a lens of considerable focal length, *viz.*, 61 cm., to avoid parallax. In the case of the study of the diffusion of proteins, two quartz mercury lamps H are use for the illumination and special glass filters I which only transmit the line 366 μμ are inserted between the lamps and the diffusion cell. The lamps are enclosed in water-cooled housing to protect the thermostat from the heat radiation. Under the influence of the strong ultraviolet illumina-

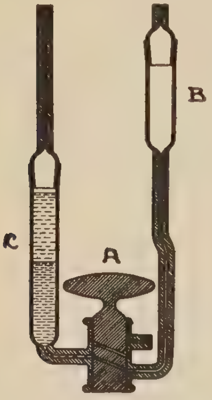

FIG. 10.—Diffusion cell.

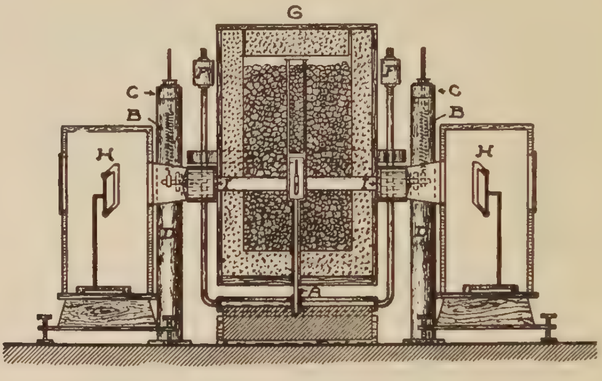

FIG. 11.—Diagram of diffusion apparatus.

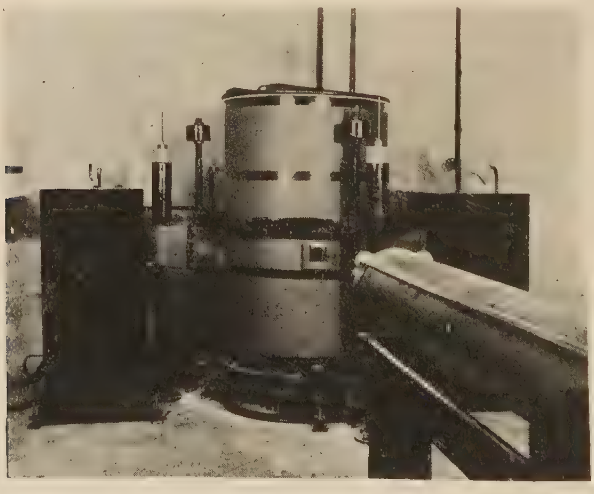

FIG. 12.—Diffusion apparatus.

tion many proteins fluoresce strongly. Pictures of the fluorescence are taken during the diffusion, and if by special measurements the relation between intensity of fluorescence and concentration of the protein is known, the variation of concentration with height in the diffusion column can be computed from microphotometric records of the pictures.

Fig. 12 gives a view of the diffusion apparatus.

As an example of the procedure Fig. 13 gives the fluorescence photograph of a 4.5 per cent egg-albumin sol, A at the start and B after 32 hours. In Fig. 14 the microphotometric record of B is reproduced and in Fig. 15 the concentration curve derived from it. The diffusion constant calculated by means of equations 3 and 10 is 0.041 at 0° C.

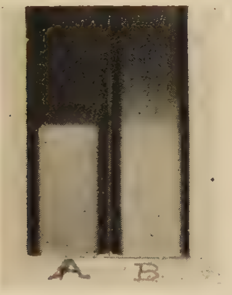

FIG. 13.—Fluorescence photography of the diffusion of egg albumin.

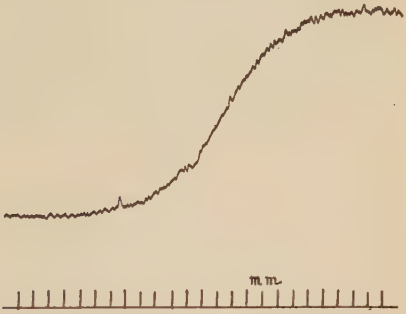

FIG. 14.—Microphotometric record of the diffusion of egg albumin.

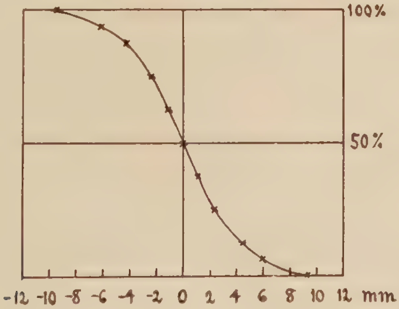

FIG. 15.—Diagram giving the relation between concentration and distance from the boundary surface in the diffusion of egg albumin.

In the case of colorless substances which do not fluoresce sufficiently, pictures may be taken by illuminating the diffusing column from behind by ultraviolet light of suitable wave length. Many proteins show a very strong absorption near the mercury line 253 μμ and light of this wave length can be isolated by means of a filter containing gaseous bromine and chlorine.[12] All parts of the apparatus through which the radiation passes must in this case be made of quartz.

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Svedberg and Fahraeus (*J. Am. Chem. Soc.*, **48**, 430-38 (1926)), measured the sedimentation equilibrium of carbon-monoxide-hemoglobin and of met-hemoglobin with the ultracentrifuge, and conclude "that hemoglobin solutions are built up of molecules containing four groups of molecular weight 16,700; that is, that the molecular weight of hemoglobin in aqueous solution is probably 66,800."

Subsidence in Colloidal Systems

By Eugene E. Ayres, Jr., Swarthmore, Pa.

Suspended particles of colloidal magnitude will settle under the influence of gravity or centrifugal force, if the mass of the particle is sufficiently large. When the mass is sufficiently small, the particles must remain always in suspension. This property of dispersoids is a function of mass alone. Mass is equal to volume times density.

The ordinary unit of measurement of colloid particles is the μ or micron, which is 0.0001 cm., or 10^{-4} cm., and the μμ, or sub-micron, which is 0.001 μ, 0.0000001 cm., or 10^{-7} cm.

Particles are often considered of colloidal magnitude only when they have a radius smaller than 0.1 μ. But there are some emulsions with globules as large as one centimeter radius that exhibit distinctly colloidal characteristics in subsidence, in the effects of added electrolytes, and in the effects of added emulsifying colloids (such as sodium and calcium soaps.) The globules in these emulsions, although huge in size, are of low mass, because their absolute density (difference between the specific gravity of the globule and the specific gravity of the medium) is very small. The globules are also well protected from coalescence by tenacious adsorbed films. These very small absolute densities are not common. Colloidal phenomena are, therefore, more frequently observed where the low mass is caused by small volume.

Ordinary filter paper holds back particles of about 5 μ; a hardened filter paper, those about 2 μ in diameter.[1] The best clay filters will retain particles larger than 0.1 μ diameter.[2] The extreme limit of microscopic visibility is about 0.1 μ. The lower limit of the ultramicroscopic is about 3 μμ. The diameter of the starch molecule is said to be about 5 μμ.[3] A fair average molecular diameter is about 1.0 μμ.

Thanks to Stokes' Law for velocity and Perrin's Law for distribution, it is a simple matter to express concretely the conditions for complete or partial subsidence. We can tell what size of particle, density, and force are necessary to make a complete subsidence possible. We can compute the time required to obtain whatever subsidence may be possible. We can go still further and compute the extent of partial subsidence for conditions where osmotic pressure is larger than gravity or centrifugal force, and we can compute the force theoretically required to move a given particle through a given depth of a given liquid in a given time.

Stokes' Law

Stokes' law for the eventually constant velocity of a particle acted upon by a constant force and moving through a medium of finite viscosity has been found to apply accurately to suspended colloids.[4, 5, 6] * The general form of the law is—

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* Stokes' law fails with very small droplets falling in air. See paper by R. A. Millikan, this volume, p. 174. J. A.

$$U = \frac{f}{6\pi r\eta}$$

where U is velocity of the particle of radius r, acted upon by the force f, while the viscosity of the medium is η

When the law is applied to particles of given mass acted upon by the acceleration of gravity, it is necessary to put—

$$f = mg$$
$$= \frac{4}{3}\pi r^3 . d . g$$

where d represents absolute density—*i.e.*, the difference between the specific gravity of the particle and the specific gravity of the medium.

Thus, we have—

$$U = \frac{2r^2dg}{9\eta}$$

Using centimeter, gram, second units, $g = 980$

$$U = 2.2 \times 10^2\frac{r^2d}{\eta}$$

This equation may be satisfactorily applied to the subsidence of colloid particles by gravity, provided the osmotic pressure opposing subsidence is inconsiderable in relative magnitude. Where the tendency toward uniform distribution is strong, the force acting upon the particle is a resultant of two opposing forces. Whether or not complete subsidence can occur depends upon this resultant.

PERRIN'S LAW

Perrin's law [7] is—

$$\log_e \frac{c_o}{c_x} = mgkx$$

where c_o is the concentration of particles at the initial level o (see Fig. 1), c_x is the concentration at the height x, m is the mass of the particle, g is the acceleration of gravity, and k is a constant equal to Avogadro's constant divided by the product of the perfect gas constant and the absolute temperature. The reciprocal of k, according to the kinetic theory, is the osmotic pressure of one particle in unit volume. Assuming a normal temperature, k is about equal to 3×10^{13} in c.g.s. units.

We may put—

$$m = \frac{4}{3}\pi r^3 d$$

wherefore

$$mgk = 10^{17} r^3 d = \alpha.$$

By computing the concentration of particles at the bottom, middle and top according to Perrin's law, it appears [8] that subsidence is measurable but far from complete when $\alpha = 1$. When $\alpha = 1$, $\frac{1}{k} = mg = f$. The osmotic pressure is equal to the force imparted by gravity. Subsidence is found to be nearly complete when $\alpha = 10$, or when the force of subsidence is ten times as great as osmotic pressure.

GRAVITY SUBSIDENCE

The criterion for subsidence may, therefore, be conveniently taken as $\alpha = 10$, or

$$r^3d = 10^{-16}.$$

When the particle is of such size and of such absolute density as to satisfy the above equation, subsidence is possible. When r^3d is smaller than 10^{-16}, complete subsidence is impossible.

Velocity, by definition, is the distance traversed in unit time. The time, τ, required to move one centimeter is $\frac{1}{U}$.

$$\tau = 4.5 \times 10^{-13} \frac{\eta}{r^2d}$$

It is sometimes convenient to express τ in terms of α.

$$\tau = 4.5 \times 10^{14} \frac{\eta r}{\alpha}$$

when $\alpha = 10$

$$\tau = 4.5 \times 10^{13} \eta r$$

$$= 2.5 \times 10^{8} \eta \sqrt[3]{\frac{1}{d}}$$

The above is an interesting expression, for it gives the time required for the complete subsidence of the smallest particles that can settle by gravity in a liquid of given viscosity and density. If one could assume that no agglomeration or crystallization takes place in a given case, we can thus compute how long a settling must be allowed before subsidence will cease. We can also know the maximum size of the particles that still remain suspended.

TABLE I

$d =$	0.01	0.1	1.0	10.0
η				
0.001	12 days	5 days	2⅓ days	1 day
0.01	4 months	50 days	23 days	12 days
0.1	3 years	16 months	8 months	4 months
1.0	30 years	13 years	7 years	3 years
$r =$	0.3 μ	0.1 μ	60 μμ	30 μμ

Table I shows the time, thus derived, for settling in liquids of various viscosities (c.g.s.). The absolute density, *d*, refers to the difference between the specific gravity of the particle and the specific gravity of the medium. At the bottom of the table is shown the maximum size of particles still remaining in suspension.

CENTRIFUGAL SUBSIDENCE

For the most part, the extension of the foregoing theory to the centrifuge is without complications.

Perrin's law requires suitable modification [9] to take into account the increase in centrifugal force as the distance is increased from the center of rotation.

By computing equilibrium in a one centimeter depth of liquid in a rotating tube 2 centimeters in radius (see Fig. 2), it develops that subsidence should be complete when $mkFg$ is 10 or greater, where F is the centrifugal force at the periphery ($x = o$) in terms of multiples of the force of gravity. If the centrifuge develops a force one hundred times the force of gravity, $F = 100$. The criterion for centrifugal subsidence is, thus, that the centrifugal force urging subsidence is ten times as great as osmotic pressure opposing subsidence. This may be expressed by

$$\beta = mkFg = 10^{17} r^3 dF = 10$$

or

$$r^3 dF = 10^{-16}$$

Over the entire one centimeter depth of liquid in Fig. 2, the mean force will be the arithmetic mean of forces from $x = 1$ to $x = O$. This is 0.75 Fg.

Mean velocity is therefore—

$$U = \frac{1.5 r^2 dFg}{9\eta}$$

$$\tau = 6 \times 10^{-3} \frac{\eta}{r^2 dF}$$

or

$$\tau = 6 \times 10^{14} \frac{\eta r}{\beta}$$

when

$$\beta = 10$$

$$\tau = 6 \times 10^{13} \eta r$$

and

$$\tau = 3.5 \times 10^{8} \eta \sqrt[3]{\frac{1}{dF}}$$

The above expression shows the time required for as complete subsidence as may be obtained with centrifugal force in a liquid of given viscosity and density.

Table II shows the time according to this formula for various viscosities and densities, when the centrifugal force is 50,000 times the force of gravity. This is the highest force now commercially applied.

TABLE II

$d =$	0.01	0.1	1.0	10.0
η				
0.001	5 hours	3 hours	1½ hours	30 min.
0.01	2½ days	30 hours	15 hours	5 hours
0.1	25 days	14 days	7 days	2½ days
1.0	8 months	4½ months	2 months	22 days
$r =$	5 μμ	3 μμ	1½ μμ	0.5 μμ

A force of 50,000 times gravity reduces the maximum time of settling in water ($\eta = 0.01$) when the particles have a specific gravity of 1.10 ($d = 0.1$) from 50 days to 30 hours, while at the same time the size of particles left in suspension is reduced from 0.1 μ to 3 μμ.

Application of Theory

A number of convenient formulæ may be readily derived from the foregoing. For example, the radius of the particle that will settle through one centimeter in one minute is—

$$r = 8.5 \times 10^{-3} \sqrt{\frac{\eta}{d}}$$

A particle whose specific gravity is 1.10 ($d = .1$) should settle through one centimeter of water ($\eta = .01$) in one minute when the radius of the particle is 25 μ.

A similar expression for the centrifuge is—

$$r = 10^{-2} \sqrt{\frac{\eta}{dF}}$$

In the above example, the particle under a centrifugal force of 50,000 times gravity would have a radius of 0.14 μ.

To compute the centrifugal force necessary to settle a particle through one centimeter in one hour—

$$F = 1.6 \times 10^{-16} \frac{\eta}{r^2 d}$$

In water ($\eta = 0.01$), when the particle has a specific gravity of 1.10 ($d = 0.1$), the force corresponding to various sizes of particles is as follows:

r	F
0.1 μ	1,500
60 μμ	5,000
40 μμ	10,000
20 μμ	40,000
10 μμ	150,000
6 μμ	500,000
4 μμ	1,000,000
1 μμ	15,000,000
0.1 μμ	1,500,000,000

At first glance, it is surprising to see how a slight decrease in the size of the particle must be accompanied by such a marked increase in centrifugal force.* A starch molecule (5 μμ) in water would require a force about one million times the force of gravity. Most molecules would require a billion and a half times gravity. These forces are far beyond the possibilities of any machines at present available.

Practical Considerations

Gravity subsidence is complicated by two disturbing factors: (1) convection currents, which interfere with subsidence, and (2) agglomeration crystallization, which, by increasing the mass of individual particles, accelerates subsidence.

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* This is because at this stage, a slight decrease in size means a large increase in kinetic motion. See paper by J. Alexander, this volume. J. A.

Convection currents are difficult to avoid. Various investigators of equilibrium in dispersoids have obtained results conforming to theory only when they have used capillary tubes. On a larger scale, the best we can do is to put the liquid in a vessel or some material of low radiation powers, keep the vessel completely surrounded by an atmosphere of even temperature and to protect from light or other radiations.

Any discussion of agglomeration or crystallization is outside the scope of this chapter. We may mention, however, the interesting fact that electric charges of colloid particles are said to be in all cases too small to affect subsidence, though they may greatly influence the rate of agglomeration or crystallization.[10]

Centrifugal force may be applied continuously or non-continuously. The non-continuous machines are sometimes the more convenient for laboratory manipulation, but the continuous machines are capable of extending much greater forces, and of handling practical volumes.

Convection currents are not negligible in centrifugal machines of any type, but in a continuous machine, as ordinarily used, the time of subsidence is short enough to reduce this disturbing factor to a minimum. Greater interference with subsidence is found in poor displacement, whereby each portion of liquid is not subjected to centrifugal force for the same length of time. This is a problem of machine design.

Some dispersoids that will settle within a short time by gravity cannot be settled in a powerful continuous centrifuge at normal rates. These are cases where the larger portion of the time taken for subsidence is for agglomeration. (An example is ferric hydroxide in water.) Comparisons can be properly made between gravity and centrifugal force only when agglomeration is imperceptible.

COALESCENCE

One of the problems in gravity or centrifugal subsidence of emulsions is to obtain the coalescence of settled globules. An interesting experimental fact is that the most powerful centrifuge will cause only slightly more coalescence than may be secured by gravity settling. It would seem that the sufficient condition for any coalescence obtainable is mere contact between globules. The pressure of one globule against another brought about by high centrifugal force appears to be a negligible factor.

The phenomenon of coalescence has not received mathematical analysis. Such an analysis might show a distinct advantage in degrees of centrifugal force higher than 50,000 times gravity.

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Sedimentation-Analysis and Its Application to the Physical Chemistry of Clays and Precipitates

By Prof. Dr. Sven Odén, Stockholm

Introduction

The determination of the size of small particles is based either on the counting of the number of particles in a definite volume of known concentration, or on the classical equation for the resistance, w, of a liquid of viscosity η towards the movement of a sphere of radius, r, and velocity, v, put forward in 1849 by Sir C. G. Stokes.[1]

$$w = 6\pi r\eta v. \tag{1}$$

If the moving force is gravity and a constant velocity of fall is attained then

$$6\pi r\eta v = \frac{4}{3}\pi r^3(\sigma - \sigma_1)g$$

from which

$$v = \frac{2}{9}gr^2\,\frac{\sigma - \sigma_1}{\eta}$$

$$= \frac{2(\sigma - \sigma_1)g}{9\ \eta}r^2 \tag{2a}$$

$$v = Cr^2 \tag{2b}$$

$$r = \sqrt{\frac{v}{C}} = \sqrt{\frac{1}{C}}\sqrt{v} = K\sqrt{v} \tag{2c}$$

Here g = gravitational acceleration
σ = density of the particle
σ_1 = density of the fluid, for water approximately = 1.

This is the ordinary form in which we know this equation, fundamental for the problem in question.

The first method mentioned gives us the *average* size of the particles which indeed may vary within wide limits; the latter method may be applied to the movement of a single particle directly and gives the size if the shape approaches the spherical.

For colloids in general the average size was determined by the first method by R. Zsigmondy.[2] Stokes' equation was first applied to soil particles by Sir Daniel Hall[3] in 1904, and to other colloids by J. Perrin.[4]

In systems consisting of a great number of particles, as colloid solutions in general, at first no attention was paid to the variation within a certain "dispersity," and I think that the first attention to the importance of variations from the mean value was given by the writer in 1911, when the conception of "isopsegmatic" and "anisopsegmatic" systems was developed and the various properties of such systems was demonstrated on colloidal sulphur.[5]

The method of determining the distribution was very rough, and consisted in a *separation* of certain size-groups by means of fractional coagulation with NaCl. This work was extended to colloid silver in 1912, where NH_4NO_3 was used as a coagulator.[6]

The application of Stokes' equation to systems consisting of particles of various size was made in 1911 by The Svedberg and K. Estrup,[7] who *counted* the various fall-velocities of a great number of single particles and thus obtained the first distribution-curves of systems such as cocoa-milk, gamboge-suspensions and suspensions of mercury.

For soils the *separation*-methods dividing the particles into coarse and fine fractions have been practiced since the days of H. Davy,[8] and we have got the various methods of mechanical analysis which need not be described here.[9]

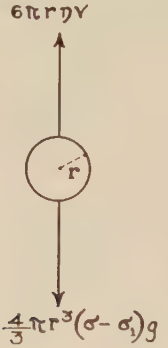

FIG. 1.

The technique of the counting-method was further developed by A. Westgren,[10] but when I tried in 1914 to get the distribution for soil particles, the method failed because the limits of size and velocity here are so wide, the latter varying from $1 \,.\, 10^{-6}$ (size 50 $\mu\mu$) to over 400 $\frac{\text{cm.}}{\text{sec.}}$ (size 1 mm.), and I began to consider other means to obtain the distribution curves, which finally led to the automatic recording balance of 1924. For soil particles and coarse suspensions the Maxwellian conception of distribution according to size was introduced[11] in 1915 though the principle underlying the experimental arrangement to obtain the distribution $F(r)$ in a then forgotten paper by Th. Schloesing, père, 1903,[12] is intricate.

In order to interpret the signification of "distribution" * we must first decide which are the most convenient variables to express the size.

Even if grouping according to velocity is more free from theoretical assumptions[13] involved in Stokes' equation, and the mathematical theory becomes simpler,[14] it is easier and more familiar to the human mind to think in terms of size than in terms of velocity, and I have therefore in this communication still kept as size variable the radius, if the particles are spheres, or the *equivalent radius* as defined by Stokes' equation if the particles are of various shapes, though we may bear in mind that what we mean with dimensions for those small particles of various shapes is quite arbitrary and perhaps better defined as a function of the velocity which we may measure direct or indirectly.

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* Probably first used by J. Clerk Maxwell to characterize physical systems, as *e.g.*, to demonstrate the different velocities of gas molecules.

The "equivalent-radius" is thus the radius of a perfect sphere of the same material that sinks through the fluid at the same average rate as the particle in question. If we thus speak of a size-interval between an equivalent radius of 1 μ to 2 μ this will give us a more clear idea of the size than if we speak of velocities from 4.10^{-4} to $1.5.10^{-3}$ cm./sec., and as long as we are not dealing with needles or thin plates, the equivalent-radius will give a fairly good idea of the real dimensions of the particles.

Stokes' equation has been extended by C. W. Oseen [15] to comprise also larger particles, and for non-spherical particles very complicated formulæ have been suggested by J. Boselli,[16] R. Gans [17] and K. Przibram [18] and others; but as we generally have to deal with particles of various kinds and shapes, no general formula can be used, and I think the conception of an "equivalent-radius" will meet with most demands in this matter.

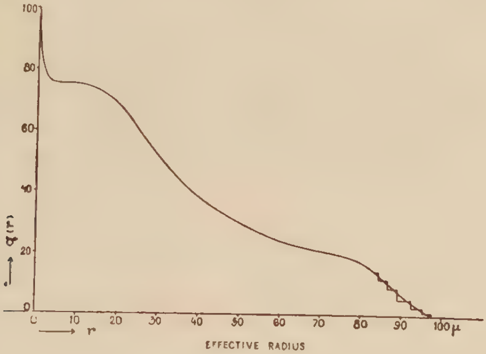


Fig. 2.

There are several ways to express the distribution graphically. In Fig. 2 are set out as abscissæ the effective radii, and as ordinates a function $q(r)$, which indicates the percentage of the sample consisting of particles larger than this effective radius. For the effective radius 0 this value is 100, for effective radius 10 μ for example, it is 75, for effective radius 30 μ, it is 50. This indicates that 75 per cent of the sample consists of particles larger than 10 μ, 50 per cent larger than 30 μ, and so forth. To obtain the percentage between any two abscissæ we have to subtract the ordinate corresponding to the larger effective radius from that corresponding to the smaller, the difference corresponding to the percentage of particles. This graphical function declines therefore from 100 for the smallest particle to 0 for the largest in the sample. If the curve is horizontal it shows that there are no particles at all in this interval. This way of representation is nearly identical with "the cumulative-curves" used in sieve-analysis,[19] and is specially convenient for the treatment of certain problems.[20] In most cases where we wish to get an idea of the bulk of the different fractions, it is a better and easier way of comprehension to represent the amounts of the particles not as a line but as a surface. This is accomplished if we define a function $F(r)$ in a way that

$$F(r) = -\frac{dq}{dr} \tag{3}$$

$$q(r_1) - q(r_2) = \int_{r_2}^{r_1} \frac{dq}{dr}\,dr = \int_{r_1}^{r_2} F(r)dr \tag{4}$$

as shown graphically in Fig. 3, where the effective radius is as before set off as abscissæ, but where we measure as ordinates, the $F(r)$ function obviously

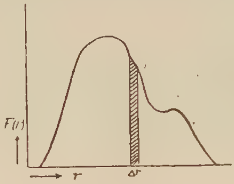


FIG. 3.

such that this value, multiplied by a part of the abscissa axis, gives us a *surface* which represents the bulk of particles in the interval of abscissæ in question. The mass of particles is here represented as an integral, and the bulk of particles between any two radius-values is obtained simply from the surface

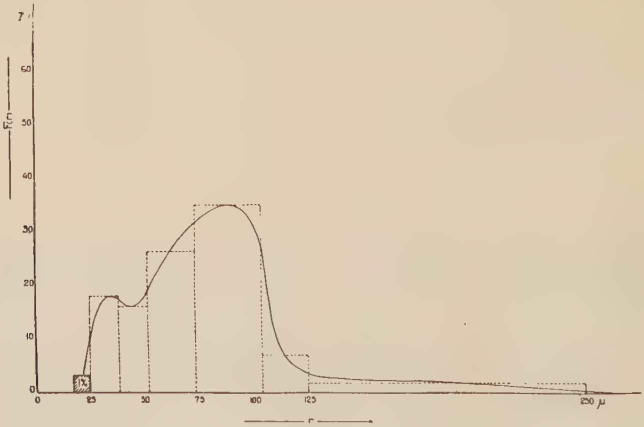


FIG. 4.

encompassed by the axis of abscissa, the corresponding ordinates, and the curve. The easiest way to carry out the graphical representation is to arrange so that the total surface comprises 100 square centimeter units on millimeter-paper, when it is only necessary to reckon the squares for each interval to arrive at the percentage.

Thus in the following $F(r)$ will denote the ordinates of the distribution function so that $F(r)dr$ means the relative amount of particles in the size interval $dr = r_2 - r_1$. In some cases when the variation in size is very great it is very inconvenient to use radii as abscissæ because of the length, but useful when graphical reproductions are desirable to have $\log_e r$ instead of r as abscissæ. It is very convenient then to multiply the $F(r)$ function by r and use as ordinates $Y = rF(r)$.

Since:

$$d(\log r).r.F(r)=\frac{1}{r}\,dr.r.F(r)=F(r)dr,$$

it is evident that the surface *content* which is proportional to the amount of particles, will not be altered from the first graphical way of expression, though the *shape* of the distribution curve will vary. This is illustrated by Figs. 4 and 5 representing the distribution curve for the same soil in non-logarithmic and logarithmic scale.

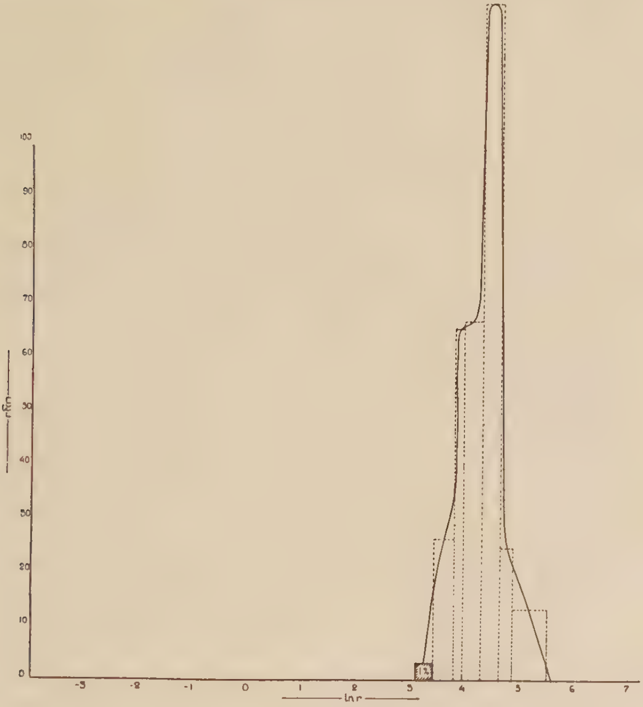


Fig. 5.

In sieve-analysis sometimes "cumulative logarithmic curves" are used, whereas abscissæ $x=$ log size, as ordinates $q=$ the percentage larger than this size.

The relation:

$$Y=rF(r)=-r\frac{dq}{dr}=-\frac{dq}{d(\log r)}=-\frac{dq}{dx} \qquad (5)$$

shows that the Y-function is the differential of these cumulative logarithmic curves.

Theory and Methods

In order to get a general point of view of the various experimental arrangements to obtain the size distribution, it is convenient to study the mathematical theory of the system: dispersed small particles and dispersion-medium, the latter usually water.

Starting with a uniform distribution of the particles obtained by thoroughly shaking the suspension, and then permitting the particles to sink with velocities depending on their various sizes, their *distribution in the liquid* as well as their accumulation rate at the bottom of the vessel will depend on the size-distribution.

The following mathematical treatment will show the relation between the distribution function $F(r)$ and certain measurable properties of the suspension.

Denoting by:

c_o = the average concentration, *i.e.* = gram solid phase per cubic-centimeter of suspension (constant).
c = the concentration at an arbitrary point (variable).
σ = the specific gravity of the solid phase (constant).
σ_1 = the specific gravity of the liquid (constant).
φ = the specific gravity of the suspension (variable).
x = the distance from the surface (variable or constant).
t = time (variable or constant).
π = the hydrostatic pressure at a depth of x and at a time t (variable).
A = accumulation at the bottom.

Thus we have

$$\varphi(x,t) = \sigma_1 + c_o \frac{\sigma - \sigma_1}{\sigma} \int_0^r F(r)\,dr \tag{6}$$

where r is a variable defined by Stokes' equation

$$r = \sqrt{\frac{x}{Ct}} \tag{2d}$$

These are the two fundamental equations from which may be derived:

(I) *The variation of the specific gravity and the concentration with the time at a definite distance x from the surface.*

Thus t is variable, x constant and:

$$\frac{d\varphi}{dt} = -\tfrac{1}{2}\sqrt{\frac{x}{C}} \cdot t^{-\frac{8}{2}} \cdot c_o \frac{\sigma - \sigma_1}{\sigma} F(r)$$

but according to (2d)

$$\sqrt{\frac{x}{C}} = r\sqrt{t}$$

thus

$$F(r) = -\frac{2\sigma}{\sigma - \sigma_1} \cdot \frac{1}{c_o} \cdot \frac{t}{r} \cdot \frac{d\varphi}{dt}$$

For $t = 0$ we have (6)

$$\varphi o = \sigma_1 + c_o \cdot \frac{\sigma - \sigma_1}{\sigma}$$

$$\therefore F(r) = -\frac{2}{\varphi o - \sigma_1} \cdot \frac{t}{r} \cdot \frac{d\varphi}{dt} \tag{7a}$$

or if

$$\frac{\varphi(t) - \sigma_1}{\varphi o - \sigma_1} = \Phi$$

$$F(r) = -\frac{2t}{r} \cdot \frac{d\Phi}{dt} \tag{7b}$$

According to (6)

$$\varphi(t) = \sigma_1 + c\,\frac{\sigma - \sigma_1}{\sigma}$$

$$\varphi o = \sigma_1 + c_o \cdot \frac{\sigma - \sigma_1}{\sigma}$$

thus we also have

$$\Phi = \frac{c}{c_o}$$

The variation of specific gravity may evidently be measured by taking out samples of definite volume and determining the dry matter thereof, M, then dM is evidently equal to $d\Phi$ and equation (2d) and (7b) may be used to calculate the distribution. *G. W. Robinson's* method [21] is of this kind, and simply consists of taking out 20 ccm. with a pipette at different times and determining the dry matter (Fig. 6). Robinson has not tried to get the distribution-

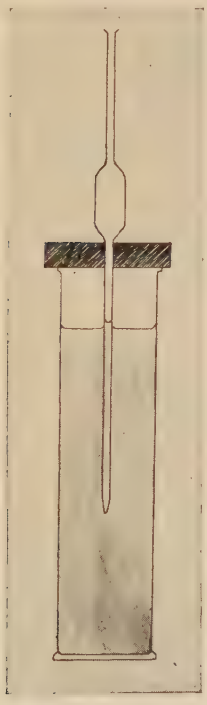


Fig. 6.

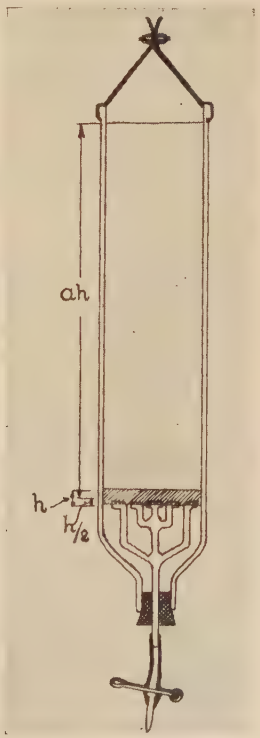


Fig. 7.

function, but determined the ordinates of what he calls "the summation curve" as functions of log*v*, that is something very similar to the cumulative-logarithmic-curve of the sieve-analysis and the *q*-function in the present treatment. The chief drawback of the method seems to be the inevitable errors in taking the samples, which from Robinson's figures seem to amount to several per cent in the single *m*-value, and therefore capable of causing large errors if the material possesses somewhat irregular distribution (Robinson, (p. 318). It is possible that these errors could be reduced by using the technique recommended by *D. S. Jennings, M. D. Thomas and W. Gardner*,[22] the essential point of which is a "multiple-mouthed pipette" (Fig. 7) through which small volumes (2 ccm.) could be sampled off with great accuracy. Like Robinson, they recommend nephelometric methods for the estimation of the quantity of particles, but since the intensity of the scattered light will vary not only with concentration but also with size and nature of the particles, it seems doubtful if this would be of much value. In the essential features similar but adapted for serial operation is *G. Krauss* method demonstrated at the 3d International Soil Congress at Prague, 1922, but not published until recently.[23]

(II) *The variation of the specific gravity and the concentration with the distance from the surface at a definite time, t.*

Thus x is variable, t constant and:

$$\frac{d\varphi}{dx} = \frac{1}{2}\sqrt{\frac{1}{Ctx}} . c_o \frac{\sigma - \sigma_1}{\sigma} . F(r)$$

but (2d)

$$\sqrt{\frac{1}{Ct}} = \frac{r}{\sqrt{x}}$$

and (6)

$$\varphi o = \sigma_1 + c_o \frac{\sigma - \sigma_1}{\sigma}$$

thus

$$F(r) = \frac{2}{\varphi o - \sigma_1} . \frac{x}{r} . \frac{d\varphi}{dx}$$

or if

$$\frac{\varphi(x) - \sigma_1}{\varphi o - \sigma_1} = \Phi ;\ F(r) = \frac{2x}{r} . \frac{d\Phi}{dx} \tag{8}$$

And as (I) also

$$\Phi = \frac{c}{c_o}$$

Evidently, determinations of the amount of solid matter at increasing depth makes equation (8) applicable. Series of such measurements have been carried out on soils by *A. N. Puri* at the Rothamsted Laboratory under *B. A. Keen's* supervision and also tested in my laboratory with promising results.

The variation of concentration with the distance from the surface were further measured by *The Svedberg* and *H. Rinde* [24] by means of measuring the adsorption of light and by *The Svedberg* and *A. J. Stamm* [71] by means of measuring the scattered light. Both methods were applied to gold hydrosols.

(III) *The variation of the hydrostatic pressure* (π) *with the time at a definite distance from the surface x.*

$$\pi = \int_0^x \varphi dx \tag{9}$$

$$\pi = \int_0^x \left(\sigma_1 + c_0 \frac{\sigma - \sigma_1}{\sigma} \int_0^r F(r) dr \right) dx$$

$$\frac{\partial \pi}{\partial t} = c_0 \frac{\sigma - \sigma_1}{\sigma} \int_0^x F(r) \cdot \frac{\partial r}{\partial t} dx$$

$$\frac{\partial^2 \pi}{\partial t^2} = c_0 \frac{\sigma - \sigma_1}{\sigma} \int_0^x \left(F(r) \cdot \frac{\partial^2 r}{\partial t^2} + F'(r) \cdot \left(\frac{\partial r}{\partial t} \right)^2 \right) dx$$

but according to (2d)

$$\frac{\partial r}{\partial t} = -\frac{1}{2} \cdot \frac{r}{t} \qquad \frac{\partial^2 r}{\partial t^2} = \frac{3}{4} \cdot \frac{r}{t^2}$$

and

and $dx = 2Ctrdr$ (t constant!).

Thus:

$$\frac{\partial^2 \pi}{\partial t^2} = c_0 \frac{\sigma - \sigma_1}{\sigma} \int_0^x C \frac{F(r) \,.\, 3r^2 + F'(r) \,.\, r^3}{2t} dr =$$

$$= c_0 \frac{\sigma - \sigma_1}{\sigma} \frac{C}{2t} \cdot \int_0^x d\left[r^3 F(r)\right] = c_0 \frac{\sigma - \sigma_1}{\sigma} \cdot \frac{C}{2t} \cdot r^3 F(r)$$

but (2d):

$$Cr^2 t = x$$

$$\therefore F(r) = \frac{2\sigma}{\sigma - \sigma_1} \cdot \frac{1}{c_0} \cdot \frac{t^2}{rx} \cdot \frac{d^2 \pi}{dt^2} \tag{10a}$$

for $t = 0$ we have (9)

$$\left. \begin{array}{ll} & \pi_0 = \sigma_1 x + c_0 x \dfrac{\sigma - \sigma_1}{\sigma} \\ \text{for } t = \infty & \\ & \pi \infty = \sigma_1 x \end{array} \right\}$$

$$\therefore F(r) = \frac{2}{\pi o - \pi \infty} \cdot \frac{t^2}{r} \cdot \frac{d^2 \pi}{dt^2}$$

or if

$$\frac{\pi(t) - \pi \infty}{\pi o - \pi \infty} = \Pi$$

$$F(r) = \frac{2t^2}{r} \cdot \frac{d^2 \Pi}{dt^2} \tag{10b}$$

By means of this equation the very simple experimental method of *G. Wiegner*[25] and his followers may be interpreted.

Wiegner's arrangement is very simple and illustrated in Fig. 8. In the big "Sedimentation tube," *A*, the suspension is poured while the stopper *D* is closed and the "measuring tube,"*C*, filled with pure water. After thorough shaking the instrument is suspended on the spurs and the glass stopper is opened. As the specific gravity of the suspension is greater than water, and the meniscus in the measuring tube is higher than that of the suspension, the difference being proportional to the pressure and the bulk of particles above the level *D*.

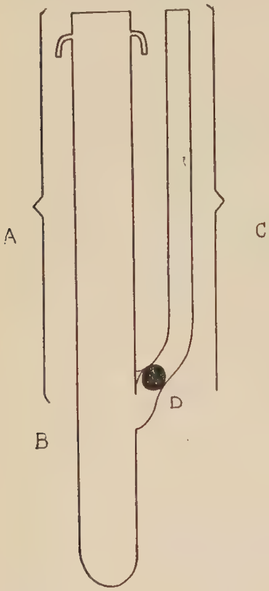


FIG. 8.

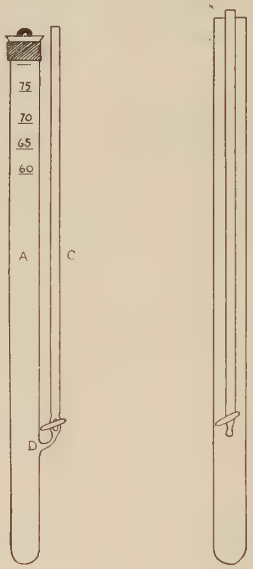


FIG. 9.

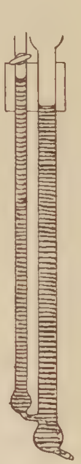


FIG. 10.

Wiegner has not used the formula (10) but calculated the percentage fraction which passes the level *D* and then made use of the same graphical method to obtain certain "sizegroups" as developed by the present writer.[11, 33] (See later below.)

Wiegner's method has been improved in collaboration with *H. Gessner* and the difference between the menisci photographed and recorded on a rotating drum.[27] (Fig. 9.)

A small variation was introduced by *Wo. Ostwald*,[28] who placed the stopper at the top instead at the bottom of the "measuring tube" (now called "Vergleichsrohr") (Fig. 10).

Wo. Ostwald has also invented another instrument called "Einschenkelflockungsmesser" and shown in Fig. 11. The suspension is poured in the bowl, *S*, and the bulb, *E*, evacuated to a certain pressure, *p*, the value of which is ascertained in a previous "test-experiment." If by means of the "threeway-cock" the bulb is put into communication with the tube dipping down into the bowl with the suspension, the latter is pressed up a certain height *X* by the atmospheric pressure, *B*. If now some particles are settling below the surface of the liquid outside the tube, and (*B*-*p*) is maintained constant, the height of the suspension in the tube will increase as the particles disappear from the suspension in the tube and the height will be a measure of the particles settled.

No attempt to obtain the distribution has yet been made by *Wo. Ostwald,* but graphical results of the settling velocity were obtained by empirical and graphical methods, and the instrument seems to be useful for a more detailed study of coagulation and aggregation phenomena. The main errors seem to arise from inevitable variations in the atmospheric pressure if the experiments are extended over any longer period, and variations in temperature effecting the pressure in *E.*

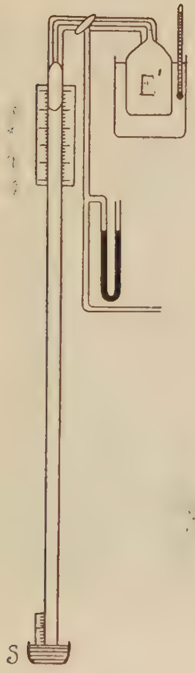


FIG. 11.

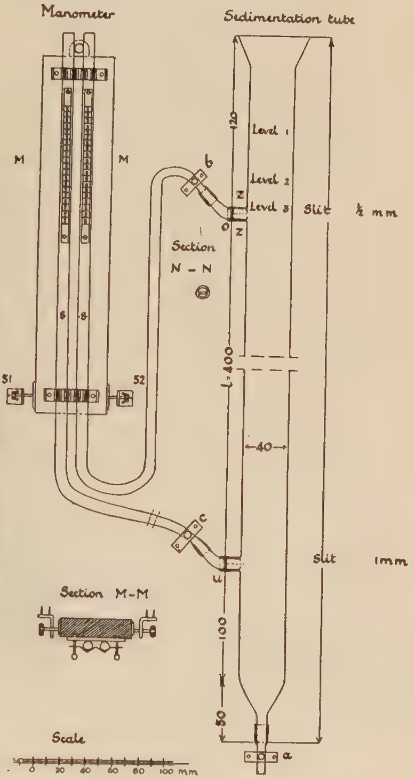


FIG. 12.

A further development, of the Wiegner method was recently made by *F. Zunker,*[29] who obtained more accuracy in the measurement of the height-difference by connecting the top and bottom layer to manometers kept apart from the instrument, thus avoiding frequently occurring errors owing to formation of foam at the top of suspensions which have been shaken violently (Fig. 12).

The great advantage of Wiegner's method is its simplicity and the cheapness of the instrument. The chief difficulties with Wiegner's apparatus are, according to my experience, the *small* variation in height between the suspension and the measuring tube, and the sensibility of the latter to variations in temperature and thereby caused expansions and contractions which introduce uncontrolled errors in the measurements. In order to increase the difference in height I have introduced pentane or some liquid of less specific gravity in the measuring-tube, and in order to avoid temperature-differences between suspension and measuring liquid, I have immersed the measuring tube ("manometer") in the suspension and made special arrangements for filling and stirring of the suspension before the actual sedimentation-measurement takes place. This kind of instrument is shown in Fig. 13 and photographs of some of these sedimentation-instruments are given in Fig. 14.

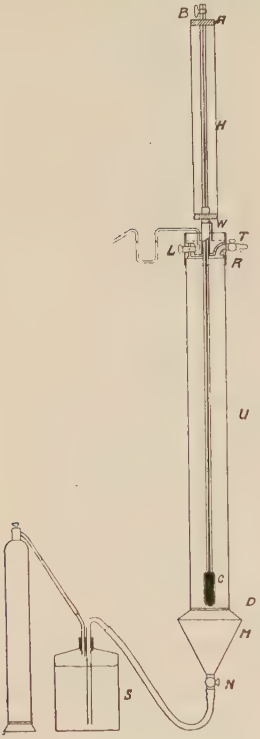


FIG. 13.

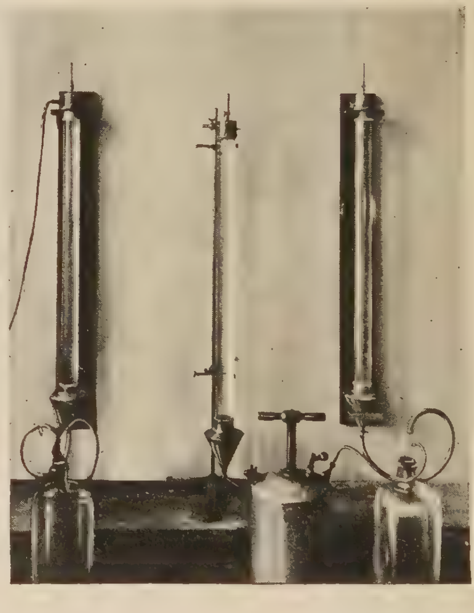


FIG. 14.

The wide glass tube *U* is fitted at its lower end into the funnel-shaped metal case, *M*, which is big enough to take up all the sedimenting particles and is provided at the bottom with a tap *N* for inlet and outlet of the suspension. The upper part of the glass tube is closed by the lid, *R*, provided with a large edge rising several centimeters and through which is inverted the manometer *AC* with its stopcock *B*. The lid is also furnished with an outlet-tube, *T*, with stopcock, thus letting out the overflow of liquid when the system is filled with the suspension, and finally a narrow channel closed by a tap, *L*, and connecting the receptacle with the sedimentation tube and a pointer, *W*, indicating the height of the water. The manometer consists of a not too narrow glass tube, *A*, etched with a millimeter scale and widened to a bulb, *C*.

at the lower part; this bulb is provided with a small hole, *D*, thus giving communication between the two liquids: the suspension outside and the manometer fluid inside the bulb. The whole device results in a kind of "communicating tubes system." Now as the particles of the suspension sink below the level, *D*, the pressure decreases and the meniscus of the manometer sinks. This causes some water to leave the bulb at the bottom, but this quantity is very insignificant since the whole displacement of fluid in the manometer-tube is only about 0.2 c.cm. The reason for having a narrow manometer tube and a bulb at the end of it is to allow a great vertical displacement of the meniscus

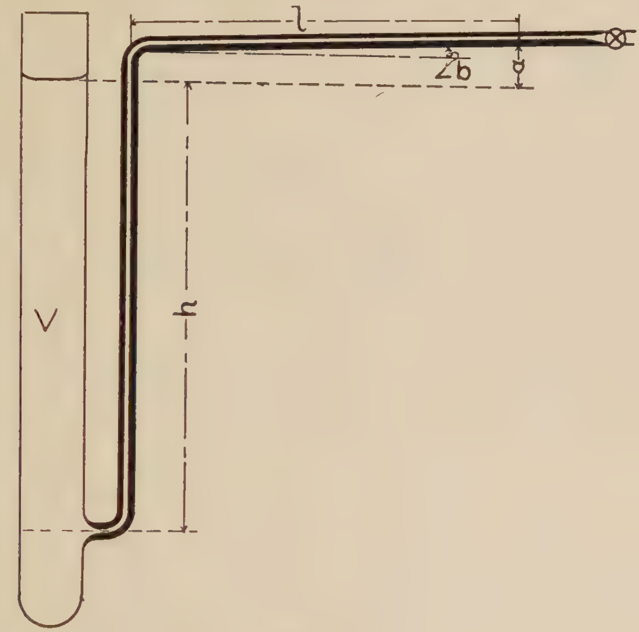


Fig. 14a.

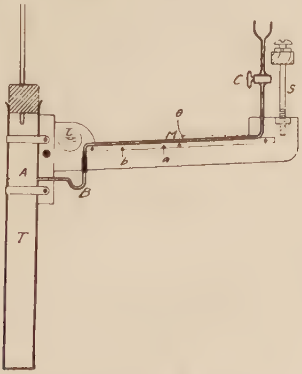


Fig. 14b.

at H as the pressure above D decreases without any considerable displacement of the surface of separation of the two liquids at D.

During the first minute there is generally some jumping up and down of the meniscus indicating currents and disturbances in the system. After the lapse of a minute we generally find a continuous sinking of the meniscus which has to be recorded as a function of the time, calculated from the moment the tap, N, is closed, these readings giving a "height-difference curve" or "pressure-curve," whose mathematical analysis may be easily interpreted graphically as will be shown further on.

A very ingenious modification of Wiegner's method was introduced by *W. J. Kelly*[64] (Fig. 14a). The measuring tube is bent in its upper part making an angle β with the horizontal. If this angle is small, a small variation in h, will correspond to a relatively large dislocation of the meniscus in the bent part. The difference in height, h, is measured in terms of the length of the liquid column in the thus nearly horizontal part of the measuring tube. If this length is l, then $h = l \sin \beta$.

The same principle has also been applied by *E. O. Kraemer* and *A. J. Stamm* in their apparatus for the study of emulsions, with the modification that the measuring tube is applied to the top of the liquid since here the disperse phase *rises* instead of settling (Fig. 14b).

(IV) *The variation in weight on an immersed body with time.*

Consider a cylinder of cross-sectional area f, whose weight in air is D and which is counterpoised in the suspension at any given time by a weight w, in a way so that the upper part is above or at the same level as the surface of the liquid. As the density of the suspension decreases on account of the removal of the particles by sedimentation, w will increase and the distribution curve can be deduced in terms of the second derivative of w with respect to time.

$$w = D - f\pi$$

$$\therefore \frac{d^2w}{dt^2} = -f\frac{d^2\pi}{dt^2}$$

Thus according to (10a):

$$F(r) = -\frac{2\sigma}{\sigma - \sigma_1} \cdot \frac{1}{c_o} \cdot \frac{t^2}{rfx} \cdot \frac{d^2w}{dt^2}$$

but

$$c_o f x \frac{\sigma - \sigma_1}{\sigma} = w\infty - w_o$$

and if

$$W = \frac{w(t) - w_o}{w\infty - w_o}$$

$$F(r) = -\frac{2t^2}{r} \cdot \frac{d^2W}{dt^2} \tag{11}$$

by means of which equation the results of *U. Pratolongo's* (1917) and *H. G. Schurecht's* (1921) experimental devices may be interpreted.

Pratolongo's device[30] consists simply in determining "the density" by means of a Westphal's balance (Fig. 15) in the top layer of the soil suspensions, as a function of time. Curves for the variation of the density with time are given, but as far as I can see no attempt to draw the distribution-curves for the samples investigated is found.

The *Schurecht* method,[31] differs from Pratolongo's method with regard to the form of the immersed plummet. The percentage of clay in suspension above the plummet is recorded as a function of *log time,* and characteristic curves were obtained for various clays, but even here no attempt to get the distribution function is made. A similar arrangement has been used in the *Polish National Institute of Agricultural Economy,* at Pulawy, and is described by *T. Mieczynski.*[63]

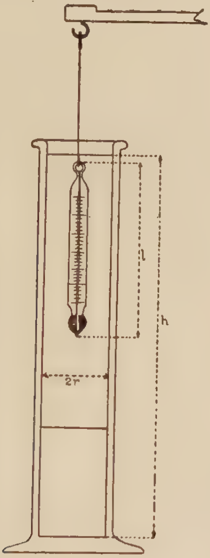


Fig. 15.

(V) *The variation of the hydrostatic pressure with the distance from the surface at a definite time.*

Thus x is variable, t constant

Equation (9)

$$\pi = \int_0^x \varphi dx$$

$$\therefore \frac{d^2\pi}{dx^2} = \frac{d\varphi}{dx}$$

Then according to II:

$$F(r) = \frac{2\sigma}{\sigma - \sigma_1} \cdot \frac{1}{c_0} \cdot \frac{x}{r} \cdot \frac{d^2\pi}{dx^2}$$

but

$$c_0 \frac{\sigma - \sigma_1}{\sigma} = \sigma_0 - \sigma_1$$

$$\therefore F(r) = \frac{2}{\sigma_0 - \sigma_1} \cdot \frac{x}{r} \cdot \frac{d^2\pi}{dx^2}$$

or if

$$\frac{\pi(x)}{\sigma_0 - \sigma_1} = \Pi$$

$$F(r) = \frac{2x}{r} \cdot \frac{d^2\Pi}{dx^2} \qquad (12)$$

An experimental arrangement seeking to make use of equation (12) and determine $\frac{d^2\pi}{dx^2}$ at distinct times was tested in the writer's laboratory in the

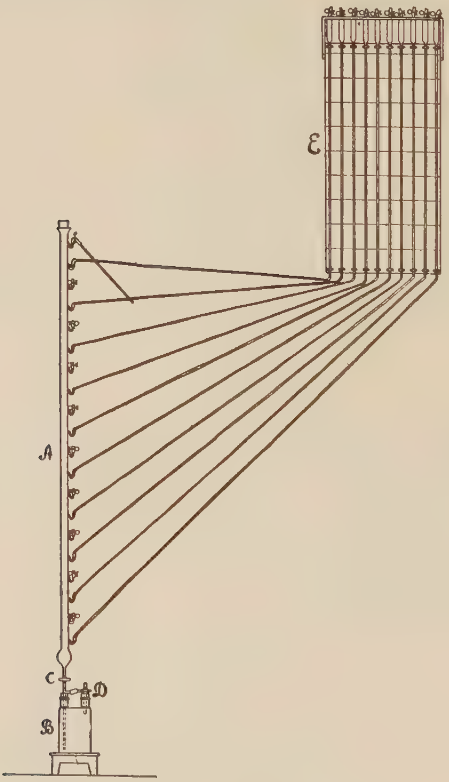


FIG. 16.

autumn 1922. A big sedimentation tube, 1.8 meter high and 5 cm. wide was connected with capillary tubes filled with pentane, acting as manometers (Fig. 16). The suspension was poured into the Woulff-flask B and pressed into the sedimentation tube, while the "manometers" were cut off by means of spring clips. After a definite time the clips were opened and the pressures read off on the scale *E*. From this a curve was drawn and $\frac{d^2\pi}{dx^2}$ graphically obtained. The experimental difficulties and errors proved, however, to be very great, mainly on account of variations in temperature between different parts of the necessarily big instrument, heat radiations from the body of the observer causing volume increase in the pentane tubes during readings, and so on, and the method was abandoned.

(VI) *Accumulation of the particles at the bottom as a function of time.*

a = accumulation weighed in water
$a\infty$ = total accumulation at complete sedimentation
f = area of the bottom

$$a = a\infty - f(\pi - \sigma_1 x)$$

$$\therefore \frac{d^2a}{dt^2} = -f\frac{d^2\pi}{dt^2}$$

Then according to III (equation 10a)

$$F(r) = \frac{2\sigma}{\sigma - \sigma_1} \cdot \frac{1}{c_0} \cdot \frac{t^2}{rfx} \cdot \frac{d^2a}{dt^2}$$

but

$$c_0 fx \,.\, \frac{\sigma - \sigma_1}{\sigma} = a\infty$$

and if

$$\frac{a}{a\infty} = A$$

$$F(r) = -\frac{2t^2}{r} \cdot \frac{d^2A}{dt^2} \tag{13}$$

This was the first equation developed 1914 by Nils Zeilon and the writer [11] which enabled the construction of the distribution curves, though the principle is intrinsically in a paper by Th. Schloesing, père [12] (1903). The experimental methods applied to this equation are still the most accurate, since the variation in the measured quantity is several hundred times greater than the accuracy of the measurement.

Schloesing's experimental arrangement (Fig. 17) consists in carrying away the deposits which accumulate at the bottom of a separating funnel, *A*, by means of a slow current of water. The soil suspension is shaken and poured into the vessel *A*. The orifice, *d*, is at the same level as the surface at *n*, and each drop which falls from the Mariotte's flask, *F*, causes some fresh water to enter the top of the funnel and some turbid water to leave at *d*, the latter carrying away the deposit and collecting it in small boxes which are moved by a clock-work.

It is evident, as Schloesing himself stated, that this arrangement contains several errors of importance. Some sediment adheres to the walls of the funnel at the bottom and is not carried away; further, the liquid which carries the sediment away is not water but suspension and contains a certain amount of smaller particles, etc. Schloesing's theoretical argument and calculations have been discussed in other connection,[32] and while in general correct, contain some errors which are functions of the distribution; but these seem to have been less than his experimental errors and escaped observation. Schloesing also added evidence to show that the sedimentation results were independent of the absolute weight and absolute concentration of the soil suspension between certain critical limits. This was confirmed by the writer [11, 33] and by Wiegner.[25]

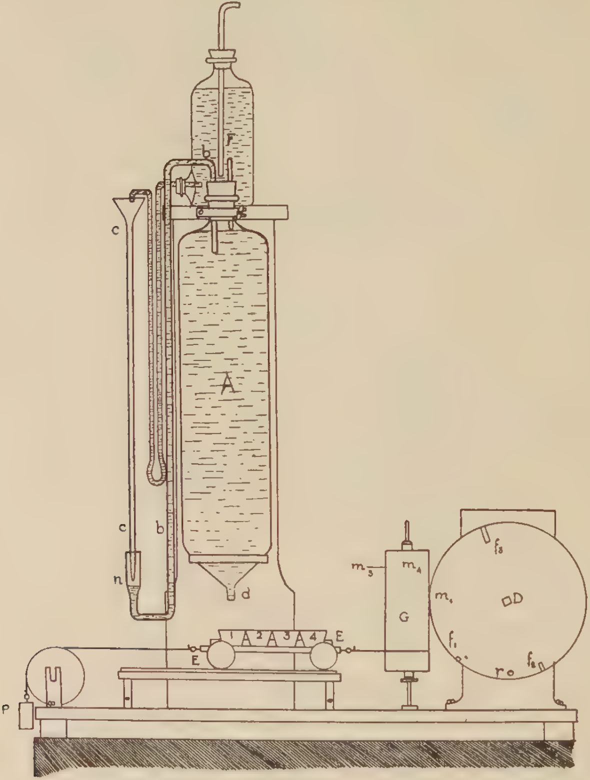


FIG. 17.

My own first experimental arrangements consisted of a sedimentation cylinder, near the bottom of which was suspended a thin plate attached to one arm of a sensitive balance (Fig. 18). When the soil suspension was poured into the cylinder the particles began to settle on the plate and the weight increased, causing the balance to move and close an electric current, by means of which a small ball was loaded on a pan attached to the other arm of the balance. The times for equal small increases in weight were determined and from this "accumulation curve" the second differential was graphically obtained and $F(r)$ calculated according to equation 13; or a graphical method was employed by means of which differences in $F(r)$ could be obtained for distinct intervals of r. The successive improvements of this instrument are visible from the figures and photographs 18-20 and are described in the original

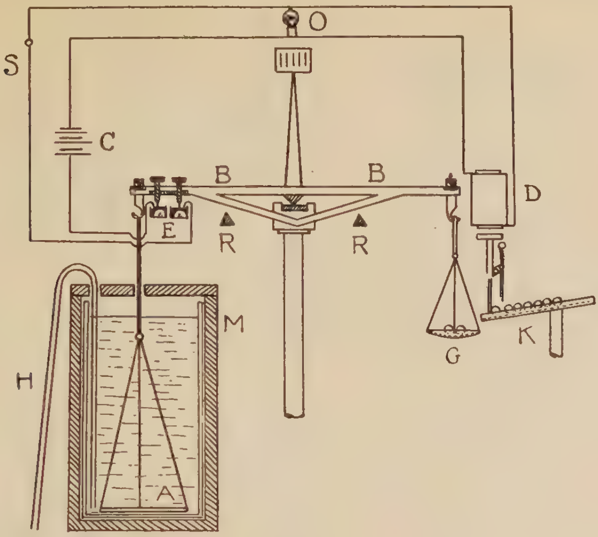


Fig. 18.

papers.[34] Similar arrangements were employed by *H. Green*[35] and by *K. Sundberg*[36] and the method proved to be useful for the study of the formation of precipitates and colloids, as well as for geological questions. These applications will be demonstrated further below.

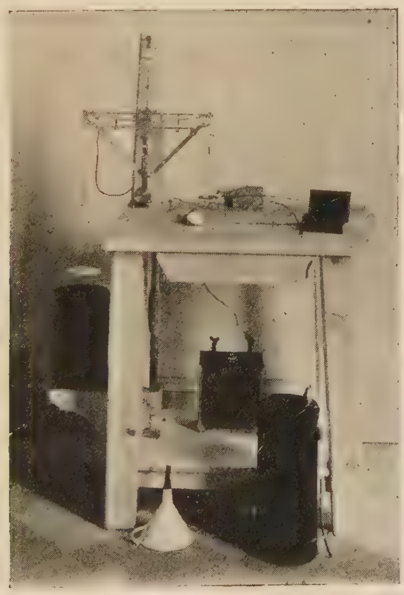


Fig. 19.

The Svedberg and *Rinde*[24] improved the sensibility of the balance and in-

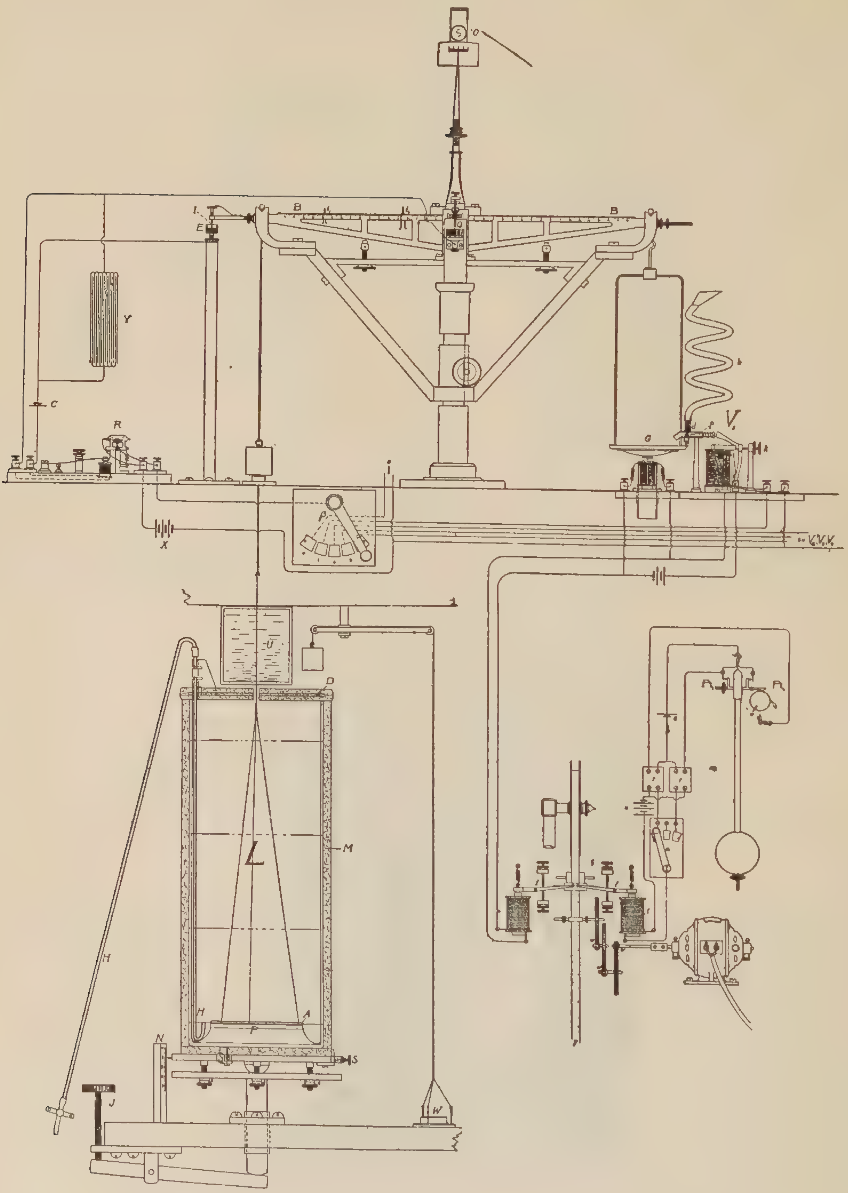


FIG. 20.

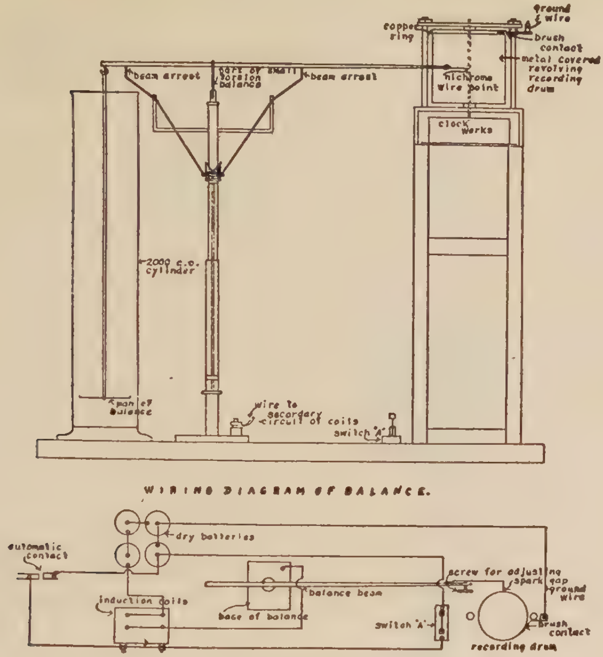
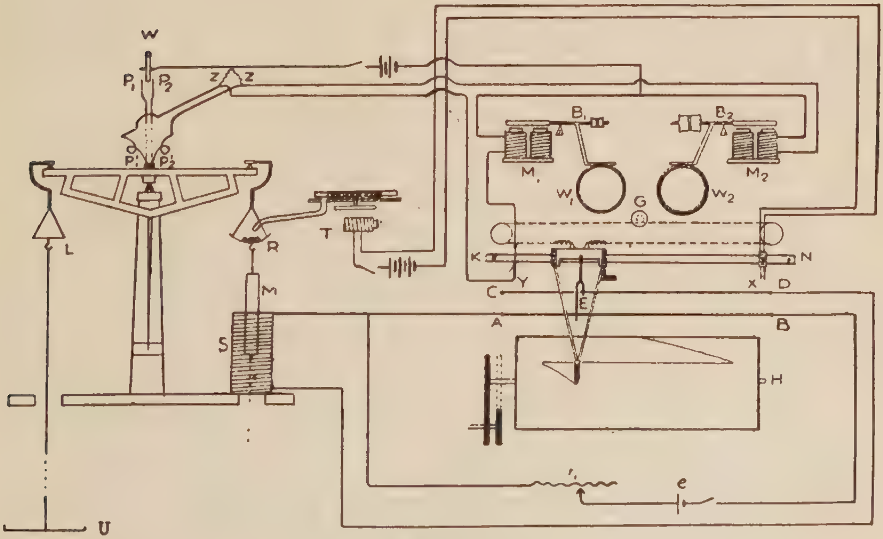

ground & wire
copper ring
brush contact
metal covered revolving recording drum
beam arrest
part of small torsion balance
beam arrest
nichrome wire point
clock works
2000 c.c. cylinder
pan of balance
wire to secondary circuit of coils
switch "A"
WIRING DIAGRAM OF BALANCE.
dry batteries
automatic contact
induction coils
base of balance
balance beam
screw for adjusting spark gap
ground wire
switch "A"
brush contact
recording drum

FIG. 21.


W
P1
P2
Z
Z
P'1
P'2
L
R
M
S
U
T
B1
B2
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W1
W2
G
K
N
Y
X
D
C
E
A
B
H
r1
e

FIG. 22.

troduced electrical control of the weighing, and Harlan W. Johnson found a way [37] to register the movement of the balance by making one arm very long and register its way on a rotating drum by means of frequent sparks jumping over from a pointer at the end (Fig. 21). By this arrangement, however, the sedimentation pan does not hold its position during the sedimentation, and the path of the particles increases as the experiment goes on.

Independently of this, the physical laboratory at Rothamsted under the direction of Dr. B. A. Keen started (1921) in collaboration with the Cambridge & Paul Instrument Co. and the writer, a series of experiments in order to construct a registering balance for chemical use with a wide range of accuracy and great sensibility. This balance * consists [38] (Fig. 22) of a suspended plate, *U*, attached to one arm of a balance, which is kept in equilibrium by an automatic adjustment of the current through a solenoid, *S*, attracting a permanent magnet *M* suspended from the second arm of the balance. When the weight of the sediment reaches a given amount, *i.e.*, when the solenoid-current reached a given value, a small metal sphere is automatically (*T*) placed on the second pan of the balance, *R*, and the solenoid current returns to a smaller value. The strength of the current is recorded on a moving paper band *H*, and the operation just described results in a curve presenting a series of steps. A very open and sensitive scale can therefore be used for the curve, although the actual trace is confined within narrow limits of width. The sensitiveness of the record can be modified or increased by suitable adjustments of the component parts of the instrument. The periodic replacement of the electromagnetic attraction by the metal balls results in the sensitiveness in any given experiment remaining constant.

Methods with Non-uniform Suspensions.

With the methods above mentioned, a homogeneous suspension always has been used, but recently methods have been developed, in which the suspension-sample is introduced as a layer at the top of the vessel, whereupon the particles must fall through the pure dispersion medium.

In 1924 *F. F. Renwick* and *V. B. Sease* [66] worked out a method of determining the sizes of the particles suspended in gelatin, which after sedimentation was congealed and prepared for microphotographic investigation. In these researches they also made use of the principle of allowing the particles to settle down from the top of the "emulsion-container," and thus their photographs show equal-sized particles at the same distance from the surface of the emulsion, the smaller ones at the top, the coarser ones at the bottom.

Further *R. Audubert* and *H. Rabaté* [67] used the same principle of sedimentation, but they obtain the rate of sedimentation by means of a procedure and apparatus of the same kind as that one used by Wiegner.

Independently of this research, *D. Werner* also worked out a very practical method of performing the sedimentation process, in which he measures the velocity of sedimentation as the velocity, with which the volume (height) of the sediment increases. Measuring the volume of the sediment instead of its weight will cause no considerable errors, since, if we consider the particles as spherical and the eventually various packing is not taken into account, the weight of the particles in a certain volume is independent of their radius. Werner's simple arrangement is illustrated by Fig. 22a. In a "mixing-room" placed at the top the sedimentation tube (which is of 1½ m. length) and separated from the latter by a tap, a concentrated suspension is introduced after the sedimentation tube (and also the tap) have been filled with the liquid. Then the tap is opened and the particles consequently begin to sink through the liquid.

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* First demonstrated at the physical-instrument exhibition in London in January, 1923.

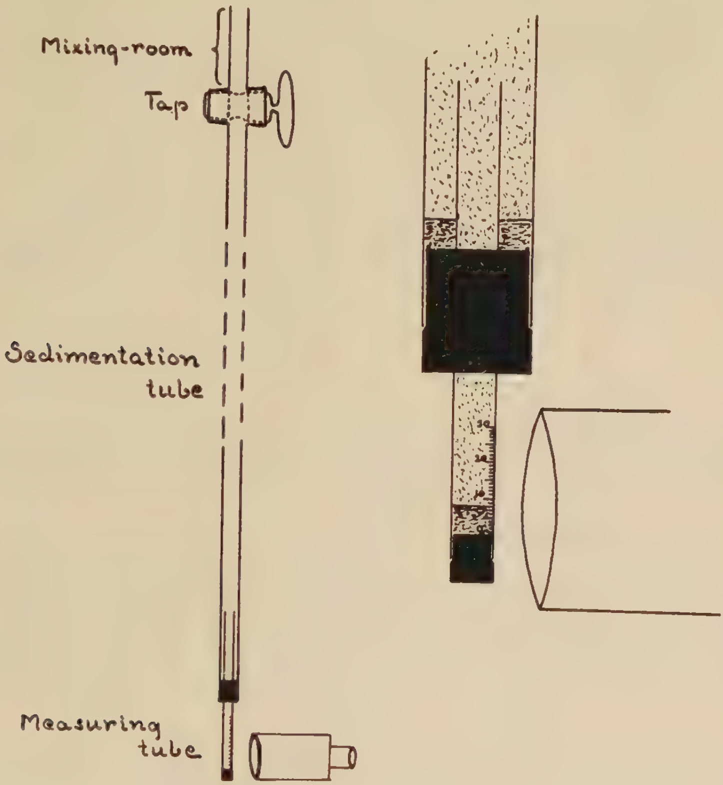

Fig. 22a.

The principle is obscurely involved in the soil analytical method known as "v. Benningsens bottle," but not developed in a way, which permits mathematical treatment. Its application to soil analysis has proved to give very accurate results.

Methods with Centrifugalization.

In all the methods previously described the moving force always was gravity. While previous investigators such as *J. Perrin* and *P. Köttgen*[62] made use of centrifugal force only in order to determine size, *The Svedberg*[24, 69, 70] and pupils have recently worked out methods of determining the size distribution by means of centrifugalization.*

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* See paper by The Svedberg, this volume, p. 838. J. A.

The Number of Particles and the Total Surface of a Sample.

From the distribution function $F(r)$ we may calculate a new function $N(r)$ of such a nature that $N(r)dr$ is equal to the *number* of particles in the interval from r to $r+dr$.[26] As before mentioned $F(r)dr$ represents the relative weight of the particles in the same interval of radii, and since the weight of one particle is $\frac{4}{3}\pi r^3\sigma$ we have

$$F(r)dr = \frac{4}{3}\pi r^3\sigma \,.\, N(r)dr$$

or

$$N(r) = \frac{3}{4\pi r^3\sigma} \,.\, F(r) \qquad (14)$$

If then $O(r)$ is a function which gives us the *surface* as a function of the radius, so that $O(r)dr =$ surface in the interval r to $r+dr$ we evidently get:

$$O(r)dr = 4\pi r^2 \,.\, N(r)dr$$

or

$$O(r)dr = \frac{3}{r\sigma} \,.\, F(r) \qquad (15)$$

Thus it is possible to obtain the total number of particles and the total surface by graphical integration of $N(r)$ or $o(r)$ from the smallest to the greatest value of r.

Geometrical and Graphical Solutions.

The essential of the mathematical deductions yielding the equations 10, 11, and 13 may be obtained in a very simple manner in the following way.

Suppose then, as before, that there is a complete disaggregation and a uniform distribution of the particles at the starting time t_0 of the experiment,

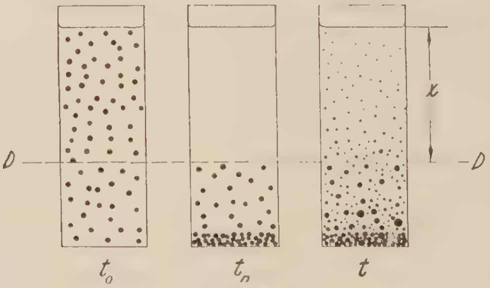

Fig. 22b.

and that the fall of each particle is independent of the others (Fig. 22b). If all particles were of the same size they should sink with the same velocity and the concentration of the particles in a certain layer D, would be constant up to a certain time t_n, since all disappearing particles are substituted by others coming from the layers above. Suddenly there would be a drop to zero at a time t_n, when the particles of a velocity $v = \frac{x}{t}$, which at the start were in the top layer, have passed D.

If on the other hand the particles are of various sizes and therefore fall with different velocities, certain groups disappear by and by completely from a certain layer, and the concentration there decreases continuously while the sedimentation proceeds.

Now consider a layer at the distance x from the surface and at the time t from the beginning of the sedimentation.

Of all the particles of various size some groups have *completely* passed below this level and dropped down in the receptacle, namely those whose velocity is $> \frac{x}{t}$ (let us call these G) while from the other groups with velocities $< \frac{x}{t}$ there has been a constant flow of particles during the whole time t altogether proportional to the time and concentration (let us call this portion S).

If we in the Fig. 23 let the ordinates of the curve OAU represent the percentage amount of particles $(G + S)$ that have passed this level (and express this quantity in relation to the total sedimented quantity, $A\,\infty$, or $y = \frac{A\,.\,100}{A\,\infty}$,) as a function of time as abscissæ, thus $y = A(t)$, then evidently $100\text{-}A(t)$ or an ordinate drawn downwards from VU, will be proportional to the quantity of particles suspended above this level.

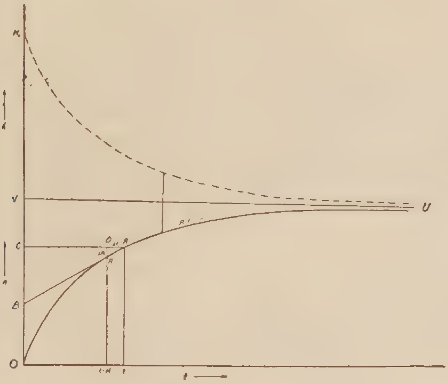

FIG. 23.

Let us now draw a tangent to the curve through the point A corresponding to the time t and through the point A_1 likewise on the curve and infinitesimally little before the time t a line A_1D parallel to the ordinate-axis and likewise AC parallel to the axis of abscissæ.

From construction and figure it follows that:

$$\frac{BC}{AC} = \frac{A_1D}{AD} = \frac{\Delta A}{\Delta t}$$

But AC corresponds to the time during which the smaller size-groups have continually passed the level C, and $\frac{\Delta A}{\Delta t}$ is the quantity which passes per unit of time if we neglect the coarser ones already settled.

$$BC = AC \cdot \frac{\Delta A}{\Delta t} = t\,\frac{\Delta A}{\Delta t}$$

thus represents just the quantity of the smaller groups which has passed the level C at the time t.

But OC corresponds to the total amount of particles which have passed the level and $OC = BC + OB$. Thus OB or the distance from the point of intersection with the y-axis of the tangent (drawn through the ordinate corresponding to the abscissa t) represents the sum of those particles smaller than a certain equivalent radius r_t that have completely passed the level, where r_t is defined by the equation

$$r_t = K\sqrt{\frac{x}{t}}.$$

Repeating this for another t-value we obtain another section proportional to all particles down to another r_{t_1}-value.

$$r_{t_1} = K\sqrt{\frac{x}{t_1}}.$$

The *difference* between these sections is evidently equal to the amount of particles in the particle-interval r_t to r_{t_1}, and by repeating this procedure we obtain the amount of particles between two equivalent radii as the distance between the points of intersection of the corresponding tangents on the Y-axis, when each tangent is laid through the points of the curve corresponding to

$$t_1 = \frac{K^2x}{r_1^2} \quad \text{respectively} \quad t_2 = \frac{K^2x}{r_2^2}.$$

It is worth observing that the "accumulation-curve" of equation (13), and the "weight difference-curve," are identical if all A and h values are expressed in fractions, the former of the ultimate value $A\infty$, the latter of the initial value h_o, and that the former is the image of the latter in an imaginary plane through VU.

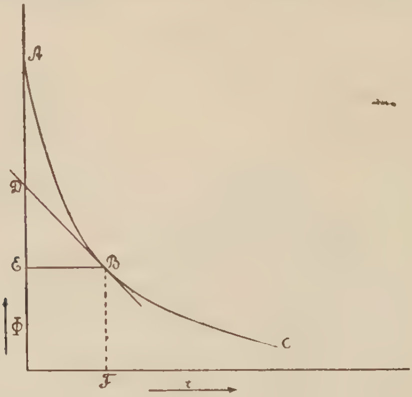

FIG. 24.

Similar graphical solutions may be developed on the basis of the other equations, and have the advantage of giving good comparison and better possibility to judge with regard to unforeseen experimental errors and disturbances.

If we for example choose equation (7) this may be interpreted as follows.

Draw a curve *ABC* with time as abscissæ, and the experimentally obtained Φ-values as ordinates (Fig. 24).

If through a point of this curve *B*, we draw a tangent (*BD*) and a line BE parallel to the axis of abscissas, the section *DE* will be equal to

$$-t\frac{d\Phi}{dt};$$

and by multiplying by 2 we obtain the value of $rF(r)$. Putting again the logarithmus of the r-values corresponding to the t-values of the tangent-points according to

$$r=\sqrt{\frac{x}{Ct}} \tag{2d}$$

and $rF(r)=-2t\frac{d\Phi}{dt}$ as ordinates, this will give the distribution curve.

The graphical solution according to the "top-layer methods" such as *Audubert's* or *Werner's* will, however, be still simpler because of the fundamentally different manner in which the sedimentation is performed. In Fig. 24a the curve *A* represents the accumulation curve for the same soil obtained from a homogeneous suspension and the curve *B* the curve obtained with the apparatus shown in Fig. 22a. In the first case the percentage of particles in the intervals r_1 to r_2 was obtained as the difference between the points of intersection of the tangents with the y-axis, drawn through the ordinates corresponding to the abscissas t_1 and t_2 as shown above. In the second case, however, the same percentage is obtained simply as the difference between the two ordinates corresponding to t_1 and t_2.

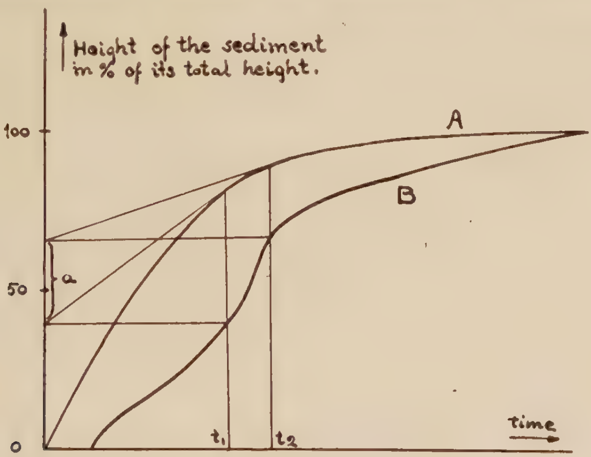

FIG. 24a.

With regard to size-intervals which the various instruments may be practically utilized, the Odén-Keen instrument is recommended in the interval from 20 μ to 0.1 μ, while the Wiegner instrument or the improved forms thereof are useful from 50 μ to 5 μ, the Jennings-Gardner method from 25 μ to 0.5 μ. D. Werner's method is applicable from 100 μ to 1 μ. On the other hand the centrifugal methods seem to be applicable from 1 μ down to 3 μμ, but all these limits may be extended in both directions by introduction of fluids with varying viscosity and specific gravity.

APPLICATIONS

1. Applications to the Study of the Structure of Precipitates.

The application of the experimental methods just described to the study of the structure of chemical precipitates was first made by the writer.[39]

It was found that when a precipitate is deposited, the particles primarily formed are coagulated, and it is generally the aggregates of a great number of primary particles which settle down at the bottom of the vessel.

How to prevent this aggregation and be able to study the structure of the primarily formed crystals is the general problem of the stability of colloid particles, a problem falling outside this treatise.

Generally we may say that at a sufficiently low concentration of the total amount of ions present in the system, it is nearly always possible to find some kind of ion which is sufficiently strongly attached to the surface of the particle to impart to the particle its electrical charge, thereby causing the particle as a whole to exert a repulsion towards other particles of the same charge, thus preventing aggregation.

This explanation does not answer the question *why* certain ions are strongly attached (adsorbed), nor which kind of forces bind the particles together in the aggregate when the electrical repulsion is diminished beyond a certain critical value.

The Primary Structure.—But having ascertained the individual freedom and stability of the particles by some stabilizing ions either beforehand present in the system (*e.g.*, $H^{\cdot}$ and OH' ions), or formed through the chemical reaction giving rise to the sediment, or finally afterwards added to the precipitate(peptization), it will be possible to study the sedimentation process, and obtain the size and size-distribution through the methods just described.

It was found in accordance with the views developed by von Weimarn[40] * that the size and size distribution will depend on:

(1) The concentration of the reacting solutions.
(2) The temperature of the reacting solutions.
(3) The presence of substances increasing or decreasing the "solubility" of the precipitate (excess of certain ions occurring in the precipitate or "acid" or "alkaline" conditions).

further depending on[41]

(4) The way in which the reacting solutions are mixed.
(5) The presence of very minute quantities (below 0.1 per mille) of poisonous substances, sometimes altering the crystal form, sometimes occurring in the crystal-lattice of the precipitate.

The last mentioned point has not been sufficiently investigated to be described here, the influence of the other conditions on the primary structure will be illustrated by the following figures, whereby in order to facilitate comparison the precipitate always was sulphate of barium.

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* See paper by P. P. von Weimarn, this volume, p. 27. J. A.

The influence of the decreasing concentration of the reacting solutions:

$$Ba(SCN)_2 + (NH_4)_2SO_4 = BaSO_4 + 2(NH_4)SCN$$

is illustrated by the three curves in Fig. 25 where the concentration varies from 0.2 molar in the curve to the left to 0.002 molar in the right hand curve. The much larger crystals and the more uniform size-distribution at a lower concentration of the reacting solutions is clearly seen. The square rectangles to the right and left indicate the bulk of particles which were either too large or too small to obtain the distribution of. In this and following figures *U* denotes the *supersaturation* or ratio between the calculated concentration at the moment of mixing, and the concentration of the saturated solution of the precipitate. The mixing was in all cases as rapid as possible.

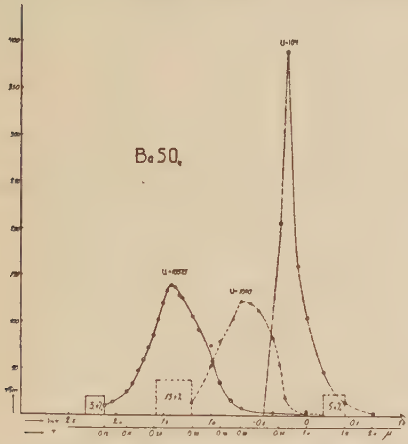


FIG. 25.

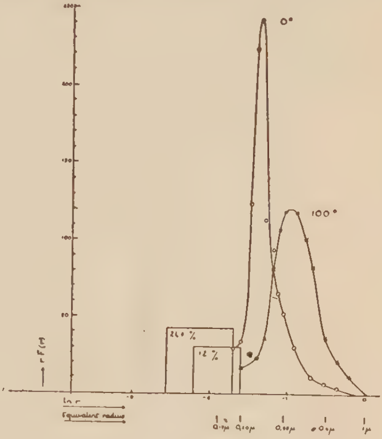


FIG. 26.

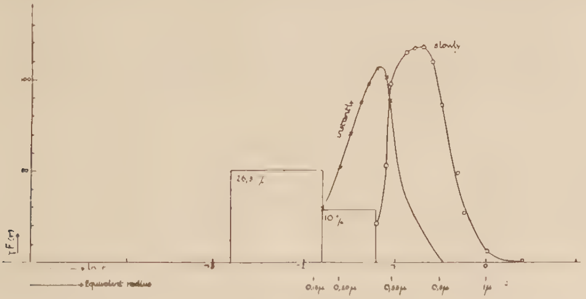


FIG. 27.

Increased temperature will make the supersaturation smaller and the precipitate coarser. This is illustrated by the two distribution-curves in Fig. 26 obtained by rapid mixing of 0.2 molar solutions of the same solutions as before but at various temperatures.

The influence of the mode of mixing on the structure is given Fig. 27. The precipitate of which the left-hand curve gives the distribution was obtained by mixing of 0.2 molar solutions of $Ba(NO_3)_2$ and $(NH_4)_2SO_4$ as rapidly as possible, whereas the curve to the right represents the distribution when the nitrate solution was dropped very slowly into the sulphate solution which was kept stirred. In the latter case nuclei the first obtained will originate from a diluted system, and therefore will not be so great in number. Further they will act as centers for the ions and molecules formed gradually as each drop of the nitrate solution is falling into the sulphate, the result being that this precipitate is of much coarser primary structure than when the nuclei are formed at once in great quantities and then grow rapidly.

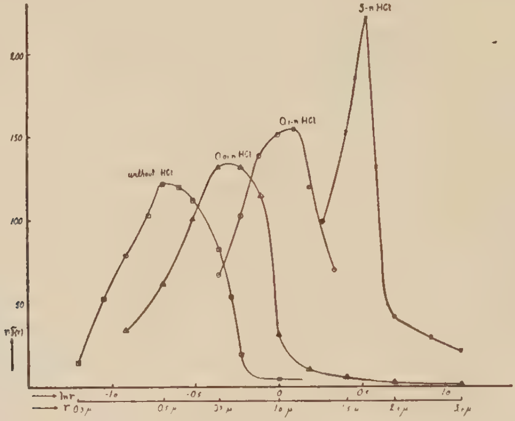


Fig. 28.

Sulphate of barium is more soluble in HCl than in water. The relative supersaturation therefore decreases as HCl is added to the system, and the well-known fact of coarser crystals when $BaSO_4$ is precipitated from acid solutions is clearly visible from the distribution curves demonstrated in Fig. 28, where the curve to the left is equal to one in Fig. 26 without any acid present during the formation, while the curves to the right give the structure at HCl-concentration increasing from 0.01 *n* to 3 *n*. Similar results demonstrated in another way were obtained by Weiser.[42]

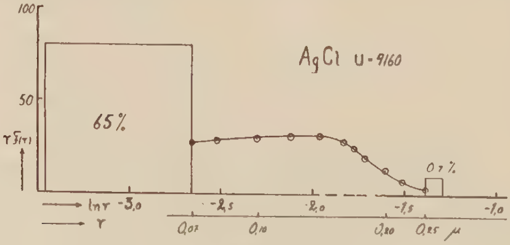


Fig. 29.

By way of example, the primary structures of some precipitates are further demonstrated in Figs. 29-36.

The structure of the silver chloride in Fig. 29 is seen to be very fine grained, almost colloidal.

The preparation was from 0.1 *n* solutions of $AgNO_3$ and KCl with an excess of the latter in order to obtain negative particles[43] which further were protected by small addition of complex chromium nitrate.[44]

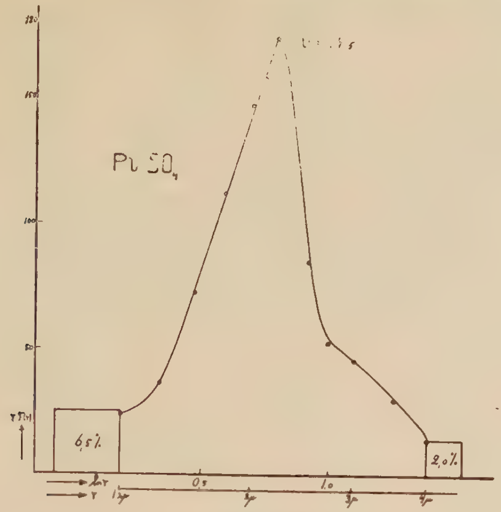


FIG. 30.

The sulphate of lead, the structure of which is represented in Fig. 31, was obtained from 0.02 molar solutions of $Pb(NO_3)_2$ and $(NH_4)_2SO_4$ mixed rapidly at 18°.

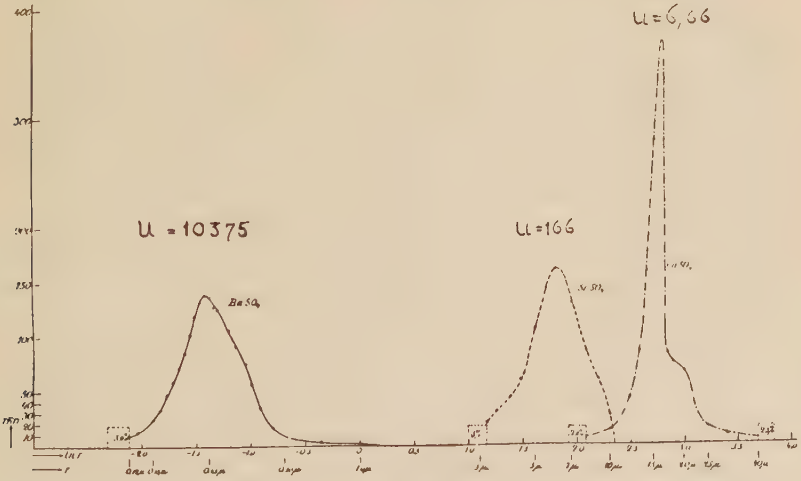


FIG. 31.

The protective electrolyte was citric acid. The three curves for $CaSO_4$, $SrSO_4$ and $BaSO_4$ in Fig. 32 show very strikingly the influence of solubility and supersaturation on the structure. The concentration of the reacting solutions was in all cases 0.2 molar.

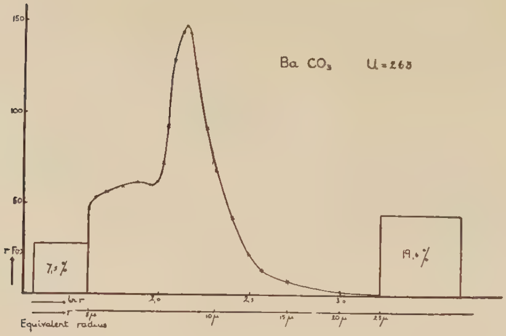


FIG. 32.

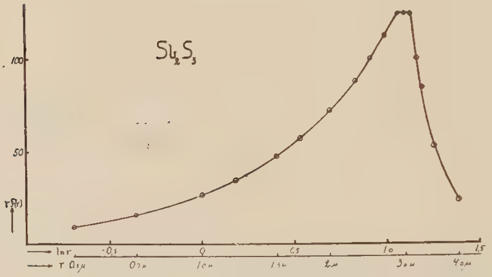


FIG. 33.

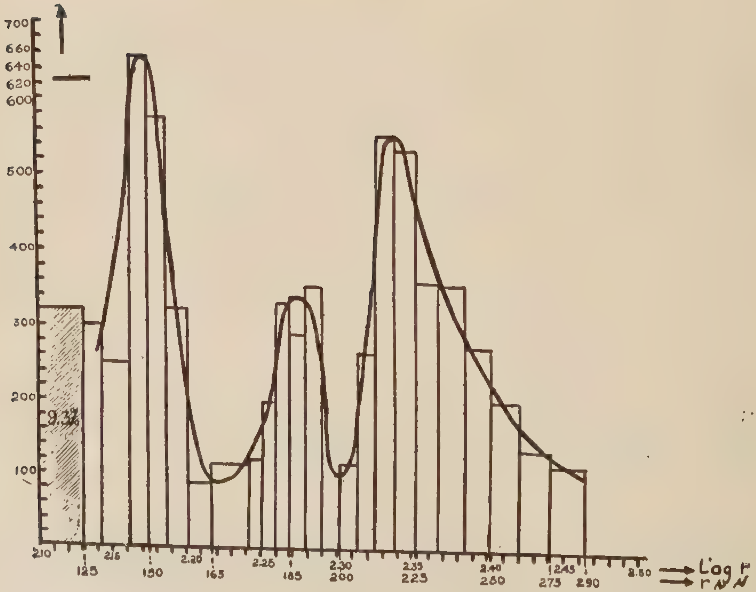


FIG. 34.

The carbonate of barium, whose primary structure is reproduced in Fig. 32, was obtained from 0.05 molar solutions of $BaCl_2$ and K_2CO_3 mixed at ordinary temperature and shaken for 10 minutes, there being meanwhile added a small crystal of citric acid, whose anion acts as peptisizing ion.

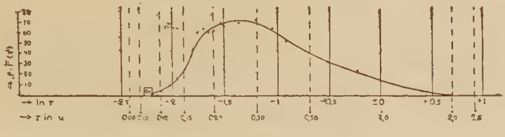


Fig. 35.

Finally Sb_2S_3 in Fig. 33 shows the structure of antimonium trisulphide obtained in the usual way, by passing H_2S through a solution of $SbCl_3$.

Some examples of the distribution in colloid systems are given in the curve, Fig. 34, representing a gold sol studied by Svedberg, and, Fig. 36,

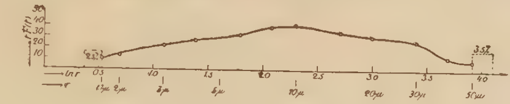


Fig. 36.

demonstrating the structure of a mercury sol obtained by Nordlund through direct current discharge in water at 50° C., and finally the colloid sulphur, Fig. 36, from Wackenroder's solution studied by the writer.

2. Applications to the Study of the Phenomena of Coagulation.

As already pointed out any explanation as to *why* certain ions are deposited on the particles, decreasing the electric charge thus causing aggregation, cannot be given here; but *when* this coagulation-process is taking place there are two kinds of phenomena occurring which may be studied by the methods under consideration: *the relative size of the aggregates formed, and the velocity with which these aggregates are built up from the primary particles.*

Taking the last mentioned point first, and using the experimental arrangement of Fig. 22 the study of the accumulation rate when electrolytes are added or result directly from the chemical reaction giving rise to the precipitate, will reveal two distinct types, which we for sake of brevity may allude to as the *reversible* and *irreversible* types, though transition forms occur.

In the diagrammatic Fig. 37, the line *OA* represents the accumulation if the primary structure is maintained; but if secondary aggregates are formed reversibly, and if they rapidly reach the size corresponding to a certain fall of potential, then the curve after a more or less short convex "growing" period, falls for a comparatively long distance *CD* as a straight line which means that the sedimenting aggregates sink with equal speed. Not until these have sedimented to *H* do the smaller aggregates sink according to the concave part of the curve *DH*.

The irreversible type is quite different, the aggregates grow during the whole time of sedimentation and the greater part of the accumulation curve is convex. After the fall of those aggregates which at the beginning were formed in the upper layers of the liquid and which during their sedimentation have taken up both primary particles and smaller secondary aggregates, a lull sets in at (R), since the lower layers have become free from particles. Only in the upper layers some particles have been left, which gradually aggregate, but do not become as large as the aggregates first formed because of the decrease of the concentration of the particles.

This "after-coagulation" is represented on the curve by the portion (REF).

A. Determination of the Time of Aggregation.—Since irreversible aggregates steadily grow, and as H. Freundlich has shown,[47] even increase more and more in the separated sediment, one cannot speak of any fixed time of aggregation for their formation, but can only consider the greater or less speed with which secondary aggregates are formed. The sharper the curvature shown by the convex curve, the greater is the speed of coagulation. But up to the present I have studied these irreversible aggregations very little. With the instruments described on p. 870 Wo. Ostwald and Fr. V. v. Hahn, however, measured the sedimentation velocity when sols of Ag_2S and Hg_2S were irreversibly coagulated with various electrolytes. Fig. 38 shows one of their results demonstrating the various stability of the two colloids, the dark shaded area being the "surface of stability" of the silver sulphide.

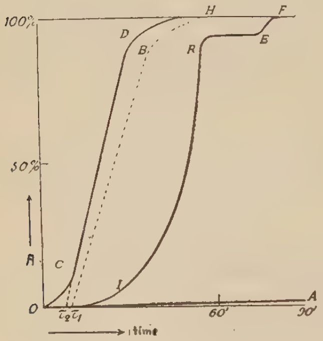


FIG. 37.

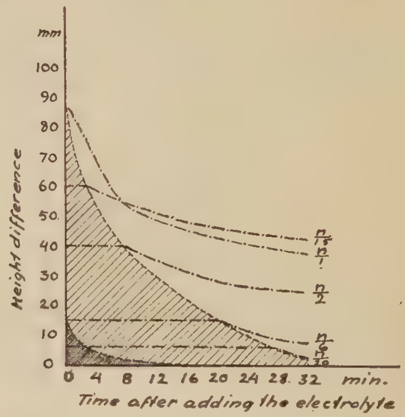


FIG. 38.

Since, on the other hand, *reversible* aggregates reach only a certain maximum size, we are able to determine the time necessary for their formation. This is obviously equal to the point of intersection (τ) of the straight portion of the accumulation curve and the axis of abscissas.

Fig. 39 shows a series of such accumulation curves for varying concentrations of the coagulator, in this case $(NH_4)NO_3$, whereby τ has been determined.

If we mark off in a diagram as abscissæ the electrolyte concentration, and as ordinates the time of aggregation (τ) thus determined, we obtain for each coagulator a characteristic curve of the same type as was previously obtained by Westgren[48] for the irreversible coagulations of Au-sols.

Westgren's research was carried out in connection with von Smoluchowski's theory of irreversible coagulation.[49] Although (τ) in Westgren's paper represents the time during which the total number of particles has decreased to one-half, and therefore does not quite correspond to the above τ, it may be of a certain interest to see how the time of aggregation at constant electrolyte content varies with the number of particles.

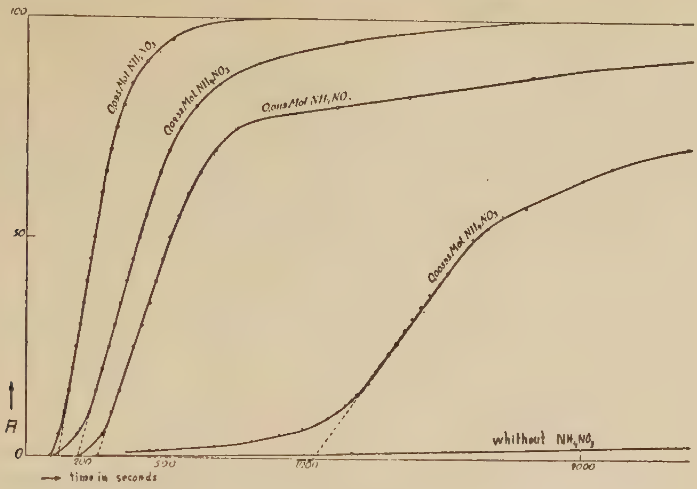


FIG. 39.

For this purpose a barium sulphate precipitate was chosen whose total particle-number in primary structure was determined to be 29.9 × 10^9 per c.c., by counting in the ultramicroscope.

As coagulator was chosen citric acid of a constant concentration of 80 millimoles per liter, at which concentration the aggregation proceeds so slowly

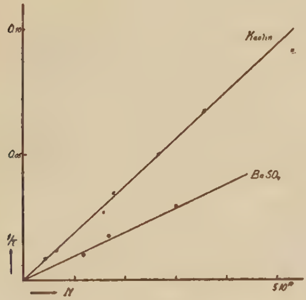


FIG. 40.

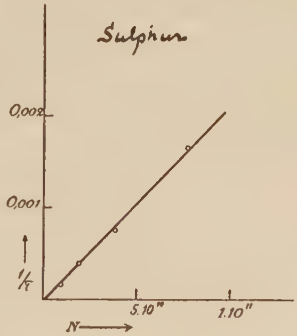


FIG. 41.

that the disturbance when pouring into the precipitation cylinder does not cause too large experimental errors. The results are marked off in Fig. 40 where the abscissæ are the number of particles and the ordinates are $\frac{1}{\tau}$; obviously we obtain a nearly straight line. This, therefore, shows that $N\tau =$ constant and is, in the case under examination, equal to about $6 \,.\, 10^{13}$ in absolute units.

This general result has been corroborated for suspensions of kaolin and colloidal sulphur as demonstrated in Figs. 40 and 41 and is in formal agreement with the von Smoluchowski coagulation formula, which suggests that the speed of aggregation in the case of irreversible and reversible aggregations is governed by similar factors.

Studying a wider range of concentration we may, however, distinguish a clear diminution of the product $N \cdot \tau$ with increasing N. The rectilinear course of the curve therefore only holds for certain intervals.

B. Relation between the Concentration of the Added Electrolyte and the Size of the Secondary Aggregates.—From the course of the accumulation curve, which is steeper and more linear the stronger the concentration of the electrolyte (Fig. 39), it follows that the secondary aggregate becomes larger as the concentration of the coagulator increases.

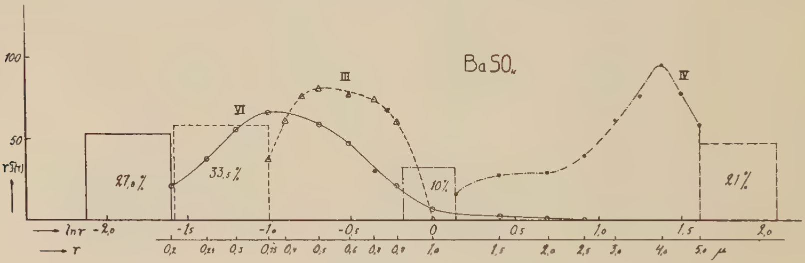


FIG. 42.

The linear course of the aggregation curve is also a *proof* that the aggregate when once grown to a certain size does not grow any more. A further proof of this has been given in the original papers.

It is even possible to a certain extent to determine the size-distribution of the secondary aggregates, as it is only with additions of strong electrolytes that they become of fairly equal size.

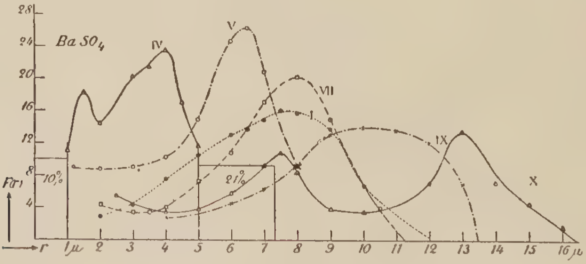


FIG. 43.

It is clear that if one takes away the time of aggregation (τ), one may on the accumulation curves (Fig. 37) from C onwards apply the same method of calculation as previously in the case of single-grain structure.

But the uncertainty and the sources of error naturally become noticeably larger in proportion as the sedimentation takes place more rapidly, and it is necessary to use larger weights to compensate the falling sediment.

Such a series of experiments, giving the secondary structure of a $BaSO_4$ precipitate for an increasing content of the coagulator NH_4NO_3 is shown in Figs. 42 and 43.

$BaSO_4$ VI. represents the primary structure of the precipitate as obtained with addition of a certain concentration of citrate.

To this suspension NH_4NO_3 to a concentration of 0.00595 moles was added, when was obtained the accumulation curve, a part of which is given in Fig. 39.

The time of aggregation can be estimated to 1040 seconds, and the straight portion corresponds to a maximum circa 0.6 μ, reproduced in $BaSO_4$ III., Fig. 42. After complete sedimentation, the solution was removed, the precipitate washed with water (but so that small amounts of ammonium nitrate were allowed to remain), then shaken with water until primary structure was reached, then treated with a new portion of ammonium nitrate, this time to the extent of 0.0119 moles, whereon the curve $BaSO_4$ IV. was registered. The time of aggregation was only 256 seconds. Here the square on the right represents the amount of particles which have fallen along the straight line with an equivalent radius of 5-6 μ.

The same curve is given in another scale on the extreme left in Fig. 43, presented in a different manner, after which follow:

$BaSO_4$ V. with coagulation concentration of electrolyte NH_4NO_3 0.0475 moles
$BaSO_4$ VII. with coagulation concentration of electrolyte....... 0.095 moles
$BaSO_4$ IX. with coagulation concentration of electrolyte....... 0.181 moles
$BaSO_4$ X. with coagulation concentration of electrolyte....... 0.362 moles

Finally, the appended $BaSO_4$ I. is of interest, as it gives us the structure as obtained *direct* after mixing of the 0.2 mole solutions of $Ba(NO_3)_2$ and $(NH_4)_2SO_4$, and then diluted with water to double volume. The ammonium nitrate formed is here present in 0.1 normal solution, and the distribution curve shows good agreement with $BaSO_4$ VII. with 0.095 normal ammonium nitrate.

The *calculation* of the number of primary particles in the secondary aggregates is of course an exceedingly precarious matter. With knowledge of the total number of particles in primary structure and the total number of secondary aggregates, a certain mean value may, however, approximately be obtained.

The Method of calculation, which has been described above, gave for 1 gram of $BaSO_4$, obtained from 0.2 molar solutions of $Ba(SCN)_2$ and $(NH_4)SO_4$ the value 6.9×10^{12} primary particles. This value has not been controlled for all the precipitates whose secondary structure are reproduced in Figs. 42, 43, and 44, but as the barium sulphate in all cases was obtained by mixing 0.2 molar solutions of $Ba(SCN)_2$ and $(NH_4)_2SO_4$, the inaccuracies are probably not greater than those caused by the variations in the methods of mixing. We may, therefore, without too great an inaccuracy, put the number of primary particles at 6.9×10^{12} for 1 gram of precipitate in all cases.

The calculation of the number of aggregates in the different cases of coagulation is more difficult. Here my reason for disregarding the 5-10 per cent for which the distribution has not been determined, is that these quantities usually represent an after-precipitate, probably originating from detached particles which during the rapid formation of the secondary aggregates have come to lie somewhat away from the centers of aggregation, and have only gradually aggregated. The fact that they have for this reason been ignored therefore makes the calculated value for the aggregates too small.

The calculation of the specific gravity of the secondary aggregates as equal to that of barium sulphate when calculating the number of secondary aggregates is, on the other hand a more hazardous source of error, as we have to deal with flakes of probably a very loose structure, including water of hydration. I have here made another calculation to show what a great influence this source of error has, the specific gravity being arbitrarily fixed at 3.00.

TABLE I

Dispersed Particles: Barium Sulphate. Electrolyte: Citric Acid

Number in the Figs.	Electrolyte Conc. in Moles/Litres	Time of Aggregation in Secs.	Value of Number of Aggregates Obtained by Integration for		Number of Primary Particles in the Aggregates for	
			S.G. = 4.5	S.G. = 3	S.G. = 4.5	S.G. = 3
LIV	0.086	3090″	$0.13 \cdot 10^{14}$	$0.08 \cdot 10^{14}$	50	80
XLIX	0.0955	2520″	$0.39 \cdot 10^{13}$	$0.25 \cdot 10^{13}$	170	260
LV	0.101	1320″	$0.27 \cdot 10^{13}$	$0.18 \cdot 10^{13}$	240	370
LVI	0.114	960″	$0.11 \cdot 10^{13}$	$0.07 . 10^{13}$	570	880
LVII	0.140	660″	$0.53 \cdot 10^{12}$	$0.34 \cdot 10^{12}$	1,200	1,900
LX	0.297	128″	$0.83 \cdot 10^{11}$	$0.54 \cdot 10^{11}$	7,600	11,700
LXI	0.395	99″	$0.22 \cdot 10^{11}$	$0.14 \cdot 10^{11}$	28,000	43,000
LXII	0.540	124″	$0.10 \cdot 10^{11}$	$0.67 \cdot 10^{10}$	60,000	92,000

With these reservations I give in Table 1 some calculations of this nature. The final column ought at least to indicate the order of magnitude of that number of particles which form the aggregates with different additions of electrolytes. They have been repeated on kaolin suspensions and colloidal sulphur.

C. In the foregoing chiefly water has been used as dispersion medium, but it is to be pointed out that various other liquids have a great influence upon the tendency of the particles of forming aggregates. Thus *D. Werner* and *G. Hedström*, who are studying the process of aggregation in my laboratory in a number of organic liquids, have found that the aggregation of SiO_2 increases as the dielectrical constant, *E*, of the liquid decreases. For example, SiO_2 in CH_3OH ($E = 31.5$) shows as well as in H_2O ($E = 81.1$) no considerable aggregation. In such liquids, however, as $(C_2H_5)_2O$, $CHCl_3$, u-C_5H_{12}, C_6H_6 and $C_6H_5CH_3$, which have an *E*-value between about 2 and 5, there appears a large number of aggregates of a sharply defined size which for the liquids mentioned nearly is the same.

D. The Reversibility of the Aggregation.—It has repeatedly been observed that the precipitates obtained by coagulation with an electrolyte in many suspensions are reversible, in so far that the coagulate, after washing free from the ions, "goes through the filters," or, if the washing is carried out in a centrifuge the precipitate breaks down and can be levigated in water.

The *degree of reversibility*, that is to say, whether it is a question of complete resolution of the secondary aggregates into primary particles, or only a partial one, now remains to be investigated.

Already several years ago I was able to show by a research carried out in collaboration with E. Ohlon,[50] that for typical reversible colloids the number of particles on repeated coagulation and suspension of the coagulate in the same volume of dispersion medium remains unchanged within the limits of experimental error, and this occurs even if one suspends the coagulate in a solution of an electrolyte, provided that the concentration of the electrolyte lies below the "critical value of concentration." This appears to indicate that the particles retain their individuality in the aggregates without any very intimate union or condensation taking place.

Since the precipitate usually consists of particles of different sizes, this sort of calculation of the number of particles before and after a reversible aggregation is unsatisfactory, because large variations in the distribution may have occurred without this having revealed itself in the determination of the mean value of the number of particles. In the experiments which are reproduced in Fig. 44 the distribution curve therefore was determined before and after aggregation, as well as the secondary structure caused by the electrolyte.

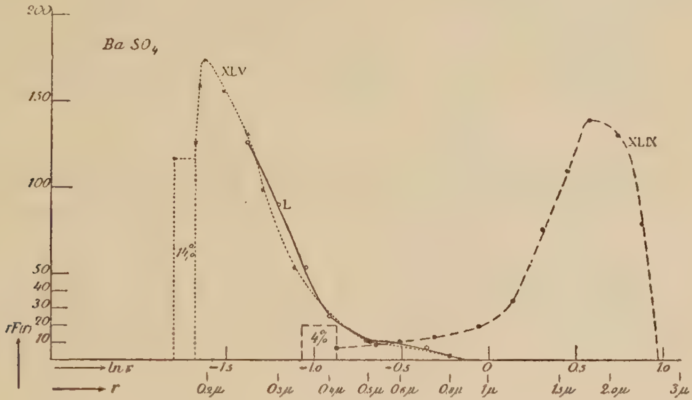


Fig. 44.

The curve $BaSO_4$ XLV. in Fig. 44 represents the primary structure for a citric acid concentration from 0.001 moles to 0.07 moles. (About = the range of critical concentration $C_1 - C_2$.) On increasing the citric acid concentration to 0.0955 moles coagulation occurred after an aggregation-time (τ) of about 42 minutes, whereupon the precipitate settled in the course of 10 hours. This secondary structure is represented by the curve XLIX.

If now to this system was added enough water to reduce the citric acid concentration to within the range of critical concentration (for $BaSO_4$ L. below 0.07 moles) values were registered which were in agreement with those of the first primary structure ($BaSO_4$ L.).

E. The Size of Secondary Aggregates is Independent of the Concentration of the Particles.—While the time required for the secondary aggregates to reach their maximum size diminishes with the increasing number of the particles per unit volume, the *size* attained by these aggregates is found to be relatively independent of the number of particles.

This can be proved by carrying out coagulations and observations with the same precipitate and at the same electrolyte-concentration, but with different heights of fall, and therefore with different numbers of particles per ccm.

Two such experimental series are reproduced in Fig. 45. These deal with the same precipitate, the primary structure of which is given in the curve XLV, in Fig. 44.

This same precipitate has in LI been given 0.08 moles of citric acid, and observations were made at 15 cm. height of fall and total volume 2420 ccm., when the number of particles immediately before aggregation amounted to 11.8×10^9 per ccm. After the precipitate had fallen completely 740 ccm. of the dispersion medium was tapped off and the precipitate vigorously shaken; observations were again made, this time with a height of fall of 10 cm. and

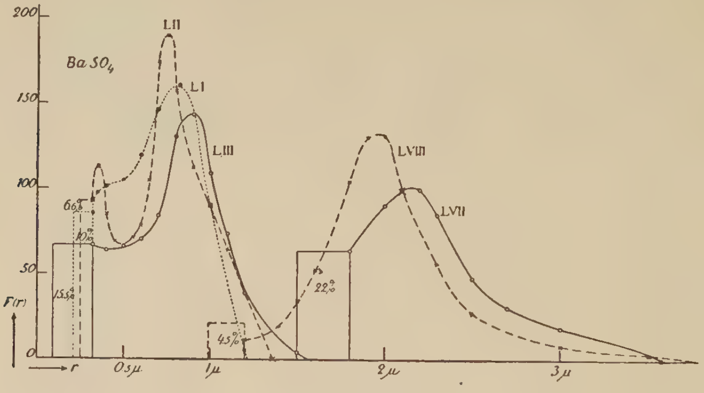


Fig. 45.

1680 ccm. volume ($N = 17.05 \times 10^9$). The curve $BaSO_4$ LII. was then obtained. $BaSO_4$ LIII. finally was obtained in a similar manner at a particle number of $N = 29.9 \times 10^9$ per ccm., by observing at a height of fall of 5 ccm. and total volume of 910 ccm.

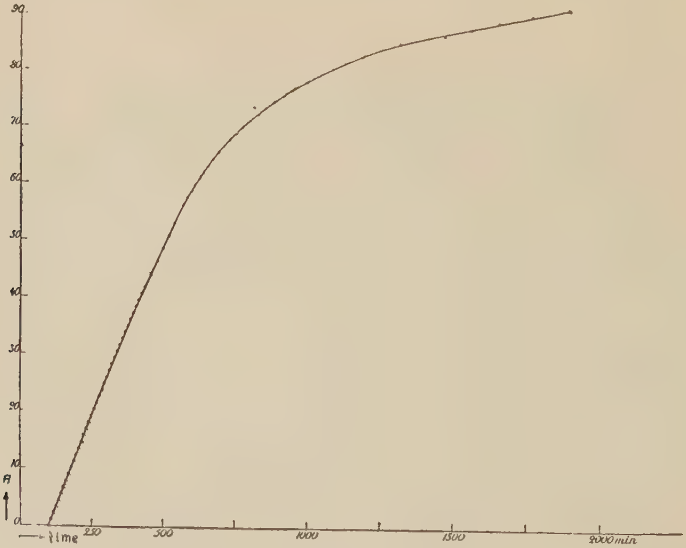


Fig. 46.

The discrepancies between the three series of observations appear most clearly in the case of the smallest aggregates. It is possible that, when shaking before each series of observations to release the primary particles, while the coagulation ion still remain in unaltered concentration, the disintegration does not proceed to completion for the very small particles, and that the irregularities are to be referred to this cause.

The important point is that for over 75 per cent of secondary aggregates between 0.6 μ and 1.4 μ the curves coincide within the limits of experimental error and that no tendency towards the formation of larger secondary aggregates is to be observed in LII compared with LI, though the particle concentration was here three times as great. In the case of LI the path of fall was 15 cm. and the largest aggregates from the upper levels had been on their way for hours before reaching the bottom. If primary particles could unite in unlimited numbers this would have been shown by the accumulation curve, which is given in Fig. 46, and which would then have shown a curvature convex to the x-axis.

Further examples showing disintegration and aggregation with increasing addition of certain electrolyte will be found in a publication to appear shortly.

3. Applications to Agricultural and Geological Problems.

The applications of the methods of sedimentation analysis to agricultural and geological problems are chiefly of descriptive and classifying nature; but

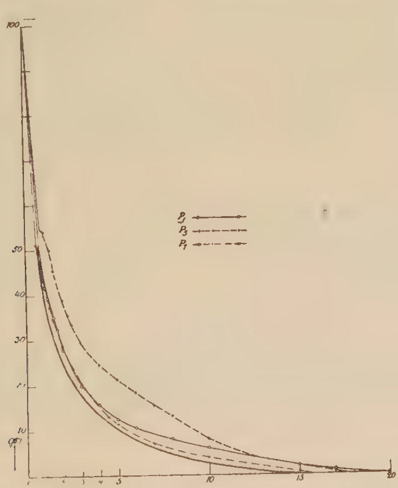


FIG. 47.

besides this some experiments on geological phenomena have been carried out and the methods have been extended to calculation of the total surface area of soils.

At first the best way to obtain a complete dispersion and disaggregation of the soil particles was studied.[51]

I recommended the method introduced by W. Beam[52] to rub the soil sample gently with a stiff brush adding ammonia water up to a concentration of 0.1 n, and then shaking the suspension for 24 hours without boiling. The comparison between various methods is most conveniently seen from the q-function and by way of example the Fig. 47 gives the difference.

The same thing is exemplified by Fig. 48 where the other way to express the distribution indicates that while boiling effectuates a disintegration in the interval 3 μ to 10 μ, it causes a considerable aggregation of the smallest particles, giving rise to aggregates of the average size 1-2 μ. For further details, see the original papers.[20] The experiments on the aggregation and coagulation of clay particles have not been completed so far as to be described in detail.[53] The same problem has been successfully treated by N. M. Comber [54] by other methods, and a comparison between our results will be given elsewhere.

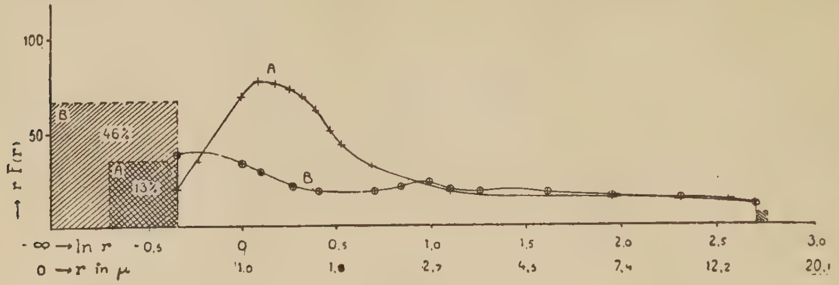


FIG. 48.

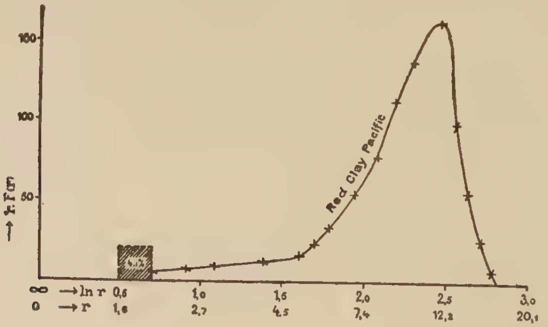


FIG. 49.

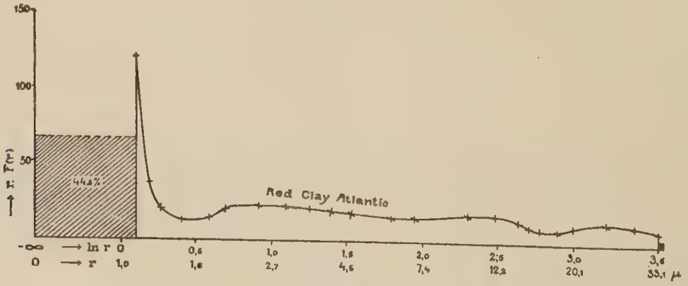


FIG. 50.

The descriptive work aiming at as complete a reproduction as possible of the distribution of the particles was begun with a study of the deep-sea deposits collected by the Challenger expedition and obtained from the late

Sir John Murray. Figs. 49, 50, 51 show the considerable difference between the Atlantic and Pacific red clay. In Fig. 51 are reproduced two globigerine oozes. These curves are of interest since they show a distinct gap in the distribution where no particles are to be found. It was found that the right hand portion consisted of the organism residues, and the left hand of inorganic clay.

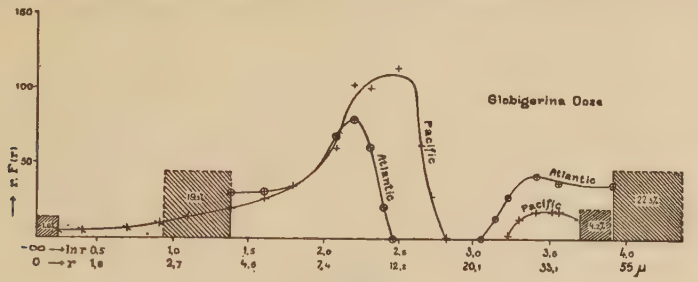


FIG. 51.

Similar minima in the distribution were obtained by G. Frödin[56] who studied the so-called (flyt-jordar) solifluction soils, *i.e.*, soils which have a tendency to flow when wetted above a certain percentage of water, especially if alkaline conditions are prevalent, as is often the case when ammonia is produced by bacteria in the spring. Then the smaller particles form a suspension or colloid solution which renders the sudden breaking down of the structure more easy, since the cementing material is taken away. One of Frödin's curves is reproduced in Fig. 52.

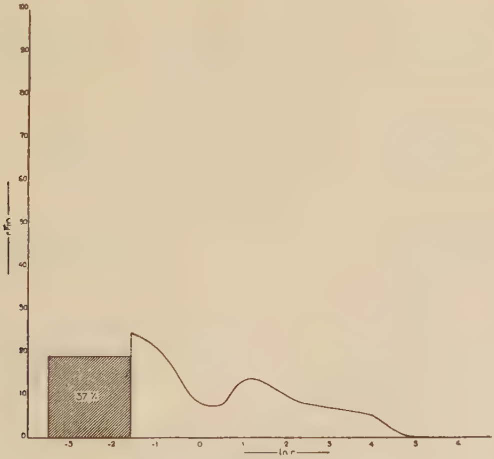


FIG. 52.

Contrary to this the casting-sands, investigated by S. Johansson,[57] showed a very marked and often sharp maximum (Fig. 53) in the distribution.

Interesting confirmation of de Geer's theory[58] with regard to the formation of the stratified Yoldia clay was obtained during the study of the structure of the various layers.

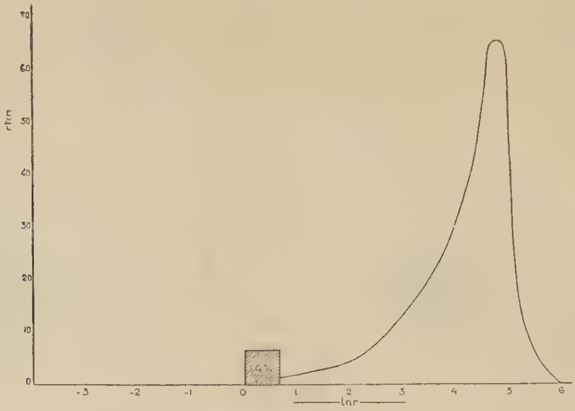
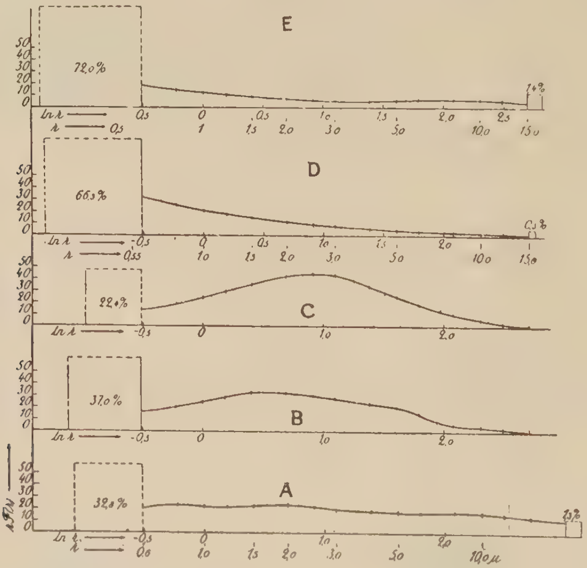


FIG. 53.

The thickness of the strata varies a great deal. The lower strata may show a thickness of several decimeters, but this diminishes as we go higher



A. A 5 cm. summer deposit.
B. „ 4 „ „ „
C. „ 2 „ „ „
D. An area where the striæ were to be measured in mm. (Summer and winter layers.)
E. An area where the striation could scarcely be distinguished, but where the clay certainly did not belong to the "stained zone".

FIG. 54.

until the thickness is not more than a millimeter, or even a fraction thereof. Higher up the streakiness disappears, and the clay takes a homogeneous gray-brown tone, with here and there a striated appearance. This brown-gray clay merges higher up into the postglacial overlying clay strata, deposited in the Ancylus Lake and the Litorine Sea.

Some of these results are reproduced in Fig. 54, showing the finer structure as the source of the deposition, *i.e.*, the mouth of the ice river from where the clay came, went further back with the ice-edge of the great inland glacier.

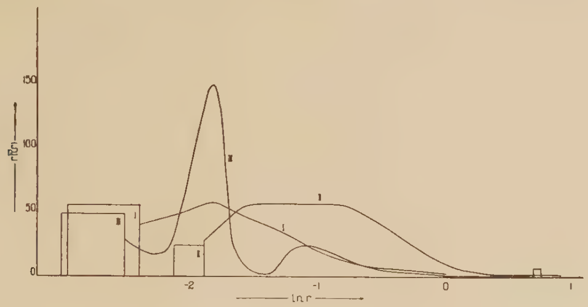


FIG. 55.

As further examples of distribution curves may be reproduced the structure of some clay-fractions from some Sudan soils investigated at the request of Dr. A. F. Joseph of the Wellcome Tropical Research Laboratories of Khartoum, Fig. 55, and a very fine-grained quarternary Swedish clay, the Ancylus-clay, specially studied by A. Reuterskiöld[60] (Fig. 56).

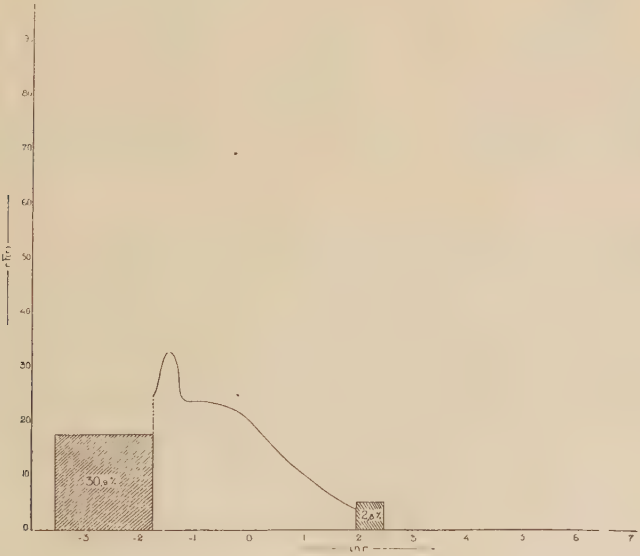


FIG. 56.

Further, a wind-deposited "loess" from Vermland (Fig. 57) and a quicksand from Vermland (Fig. 58), and as an example of a coarse sediment

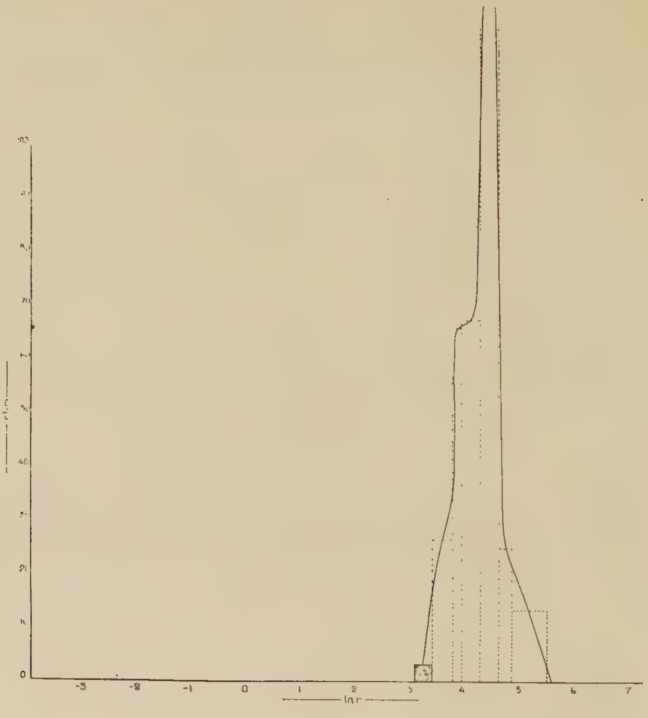

100
70
40
0
20
r f_r n
1.2
-3
-2
-1
0
1
2
3
4
5
6
7
ln r

FIG. 57.

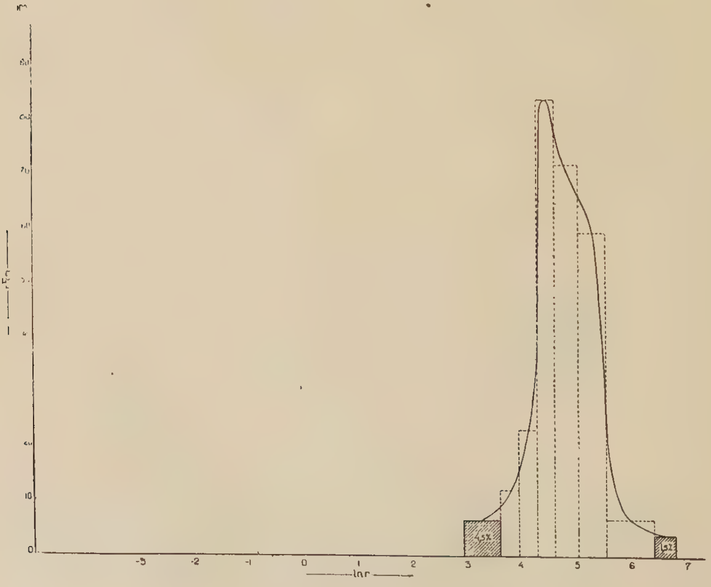

100
80
70
10
0
r f_r n
4.5%
1.5%
-3
-2
-1
0
1
2
3
4
5
6
7
ln r

FIG. 58.

studied partly by sieve analysis, partly by sedimentation analysis, I reproduce in Fig. 59 the structure of a morain from Vermland.

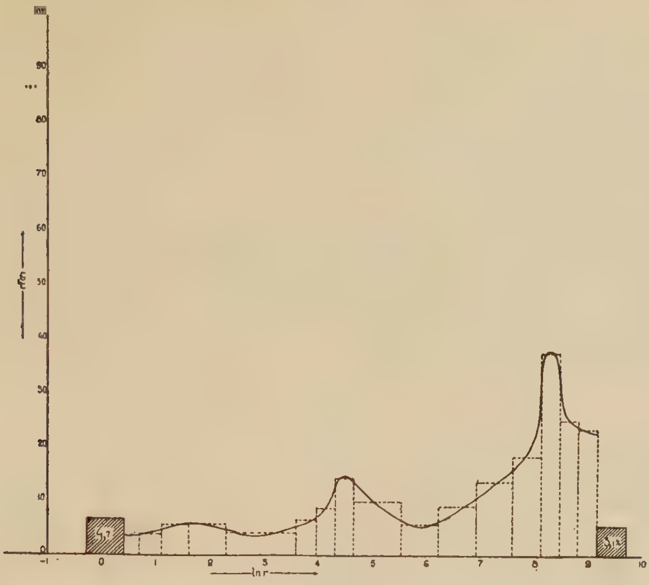


FIG. 59.

Finally, it may be mentioned that Moyer D. Thomas [61] has recently published a paper on the structure of some natural Utah soils studied by means of the Gardner-Jennings method.

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The Colloidal Aspect of Analytical Chemistry

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The following article is an extension of one by the present author on "Colloid Problems in Analytical Chemistry" which was contained in the Fourth Report on Colloid Chemistry.* Permission to make use of that article was given by the Controller of H.M. Stationery Office.

An endeavor has been made to consider all papers bearing on the subject being discussed which had appeared up to the end of 1925:

The important part that colloid phenomena play in chemical analysis has doubtless been recognized in great measure since Ostwald drew attention to the matter in 1894 in the first edition of his well-known book "Die Wissenschaftlichen Grundlagen der analytischen Chemie." There can be little doubt, however, that such phenomena play an even more fundamental part in most analytical operations than is generally realized. Much still remains obscure, but sufficient is now known about colloids and their behavior under different circumstances to give the chemist sure guidance through most of his analytical difficulties.

In what follows an attempt has been made to survey the matter as generally as possible—illustrating it with a few examples. Aqueous solutions alone have been considered. An attempt has been made to treat all the "colloidal" phenomena as being essentially due to ordinary chemical processes and explicable in terms of chemical combination and ionization. This method of dealing with the matter seems to have certain merits. It is hoped that all important matters have been considered sufficiently, to cover, in a general way, all the special characteristics of particular reactions.

THE FORMATION OF PRECIPITATES

The last stage in the formation of a precipitate is, in many cases, the coagulation by electrolytes of a colloidal solution. To what extent all precipitates pass through this, or a similar stage, seems somewhat doubtful, but a consideration of the conditions which lead to precipitation will give some clue to the probable course of events. The question of the coagulation of colloidal solutions and the re-solution or peptization of the precipitates obtained, has been considered very fully, and with a wealth of references, by Bancroft in the Second Report of the Committee on Colloid Chemistry and its Industrial Applications, 1918, pp. 2-16.

The recognition of the part played by the "solubility product" in determining the conditions under which a compound can be precipitated, is due to Ostwald; and although the law of mass action is not generally applicable to strong electrolytes, at any rate in its simple form, it does in most cases give a very useful guide. In favorable cases, such as the precipitation of sparingly soluble salts of weak acids (*e.g.*, sulphides of heavy metals) the requirements of the law are often obeyed quantitatively.[1]

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* "British Association for the Advancement of Science." Published by H.M. Stationery Office, 1922.

These results are, however, independent of the mechanism of the final stage of precipitation and would be the same whether that were of the nature of ordinary crystallization or of electrolytic coagulation.

It is the stage of precipitation prior to the actual settling out of the solid which would appear to depend directly on the solubility product, and for the present purpose it can be assumed that the law of mass action does apply to the initial stages of all precipitates.

On mixing solutions of two electrolytes, which by double decomposition can give rise to a less soluble compound, the latter will sooner or later separate from solution when its solubility product has been overstepped. The time taken for this to occur may vary greatly according to circumstances and so also will the degree of supersaturation required. It is important to bear in mind that the solubility of a substance depends upon the size of the particles. The solubility is practically independent of size if the particles are greater than 0.02 mm. in diameter, but there is a well marked increase when they become much smaller than this. When their magnitude approaches that of an isolated molecule, their solubility may be many times greater than that characteristic of large particles. It is because of this increased solubility of fine particles that in the absence of the solid phase, some supersaturation is inevitable prior to precipitation. Its degree will depend upon such factors as (*a*) presence or absence of dust or other nuclei, (*b*) physical conditions of the experiment such as temperature, rate of admixture of reactants, etc., (*c*) specific characteristics of the substance being precipitated.

The unstable supersaturated condition breaks down more or less suddenly, but the degree of suddenness varies from case to case, being influenced by temperature and many factors such as rate of movement of the solution. The well-known effect of scratching the glass walls of the containing vessel in promoting crystallization of such substances as magnesium ammonium phosphate has been ascribed by Fricke[2] to the formation of a suspension of negatively charged glass particles which act as crystallization nuclei. Dede[3] gives an electrostatic explanation of the phenomenon, however, while Fricke and Rohmann[4] have also suggested that the formation of a fresh surface or a surface partly separated from its surface film favors the separation of crystals.

A number of polymolecular nuclei now form in the solution. Their number will depend chiefly upon (*a*) the degree of supersaturation, (*b*) the suddenness with which the condition of supersaturation breaks down, (*c*) the total concentration of the compound about to separate, (*d*) the temperature—this mainly as affecting (*a*), (*b*) and (*c*).

If the individual molecules in these primary nuclei are all oriented in the same way, the latter must be regarded as being crystalline, and it seems likely that this is the case except possibly with substances of very high molecular weight.* The number of individual molecules in the primary nuclei may well vary considerably.

From the work of Perrin[5] we know that, on the one hand, such nuclei will behave like large molecules. They are able to diffuse, exert osmotic pressure, etc., in virtue of their molecular motion (the Brownian movement), which however is slow, and corresponds to their high molecular weight (that of the aggregate regarded as one molecule). On the other hand, the particles will have the properties characteristic of a sol, although probably some of these properties are the result of interaction between the nuclei originally separating out and the surrounding solution.

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* The X-ray spectrometer (Scherrer) shows that crystalline and random clusters may co-exist, *e.g.*, in colloidal silicic and stannic acid. J. A.

As soon as the nuclei appear they are subject to the influence of all the constituents present in the surrounding medium—molecules and ions of both solvent and dissolved substances. Molecules of the same kind as those present in the primary nuclei tend to attach themselves bodily and regularly, so increasing the size of the crystal which would ultimately become large enough to settle out provided no other complicating factor came into play. In many cases the minute growing crystal (which, as has been mentioned, can be regarded as a single molecule)* may be expected to have some tendency to split off one or more ions and the electrical charge, which such particles usually carry, is probably to some extent due to such ionization. This ionization probably occurs in such a way as to give one or more simple ions of small mass and a heavy residue. Whether the light ions so split off are positive or negative will depend upon the chemical nature of the ionizing particle, but this spontaneous ionization would certainly be largely influenced by other ions present in the solution, and this question will be considered presently.

That "colloidal electrolytes" exist is now well recognized, largely as a result of McBain's work on the soaps.[6] They are special cases of colloids where the electrolytic character is more marked than it is in the case of most of the colloids with which this paper deals. This is largely because the typical "colloidal electrolytes" are much less sensitive to coagulation than are ordinary colloids. They are moreover salts to which definite stoichieometric formulæ can be assigned.

It seems reasonable to think that the transition from the stage in which a substance is dissolved in the simplest molecular condition to that where it separates in the solid (or liquid) state, either visibly or ultramicroscopically, is really continuous, although the whole transition may occur over such an excessively small range as to make its actual observation very difficult. The charged (ionized) colloidally suspended crystalline particle would thus be the result of gradual polymerization (or growth) of the simple molecules. There is evidence to show that a kind of polymerization and ionization similar in character to that just imagined does occur in solutions of many salts at concentrations far below those at which even ultramicroscopic particles begin to form. There seems no reason why it should not continue right to the limit of crystallization. Cases of this kind have been investigated by Donnan and Bassett,[7] and by Watkins and Denham,[8] where the polymerization and ionization was of such a character as to give simple metallic cations ($Co^{\cdot\cdot}$, $Cu^{\cdot\cdot}$), and heavier complex anions such as $Co\,Cl_4^{\cdot\cdot}$ or $Cu\,Cl_4^{\cdot\cdot}$

Now in most cases the crystalline particle forms and grows in a solution containing simple molecules and their ions other than those which go to build it up, and it is to be expected that some interchange of ions will occur. A particle ionizing into a heavy complex cation, and one or more simple anions such as OH', Cl' or SO_4'', will exchange some of the latter for any other negative ions also present in the solution. The extent of this interchange will depend, among other things, upon the relative proportions of the foreign anions and those characteristic of the particle. This would be perfectly analogous to the process by which, for example, some K Br is formed in a solution obtained by mixing solutions of Na Br and KCl, and it would seem to be one reason for the almost constant presence of some foreign acid radicles in many precipitates. Where the particle ionizes into heavy complex anion and one or more simple cations, the latter will similarly be exchanged to some extent for other positive ions present in the solution. It will be realized that ions thus taken up by the particle may themselves be of a composite character and contain both metal and acid radicle.

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* But they *are* not molecules. This recalls Abraham Lincoln's poser: If you call a dog's tail a leg, how many legs has a dog? His answer was four; because calling a tail a leg, does not make it a leg. J. A.

The more or less ionized particles are also subject to other influences, not precisely of an ionic character, in which the solvent molecules, as also other molecules present, play an important part. Some of these various molecules attach themselves to the surface of the suspended particles—so-called surface adsorption. This has generally been regarded as a physical process, though the work of Langmuir[9] (summarizing paper in *J. Amer. Chem. Soc.*, 1916, 38, 2221) has shown that it is probably essentially chemical in nature and due to more or less marked residual affinity of the surface layer of the adsorbing particle. The work on crystal structure by Bragg and others[10] clearly shows that the atoms in the outermost layers of crystals are not fully saturated, so that such surface additions of foreign molecules need not be regarded as very remarkable. The firmness with which they are held will naturally depend both on the nature of the adsorbing particle and on that of the foreign molecules. As it is a surface phenomenon, it is only well marked in cases where the adsorbing substance is in a fine state of division. In aqueous solutions a sheath of water molecules appears to be so held, containing, however, other molecules as well.

There seems no reason why some of the molecules so held should not still ionize in more or less the usual way, which really amounts to the same thing as saying that certain ions are removed from the solution and adsorbed by the colloidal particles, which would at the same time receive the ionic charges. The usually accepted view is that the charges carried by colloidal particles originate in this way by ionic adsorption, but it seems a mistake to ignore the possibility of spontaneous ionization of the particles themselves.

The sheath of adsorbed water (or solvent) molecules round the particles in a colloidal suspension probably plays an important part in preventing coalescence and settling out when the particles collide. As a rule the particles are electrically charged in a similar manner and so repel one another, but uncharged particles can remain in colloidal suspension in some cases, and even in cases where most of the particles are charged it must be supposed that some kind of equilibrium exists between the charged particles, its ions and the uncharged particles. Some collisions between the latter probably take place therefore, and in time, even in such cases, coalescence and settling out might be expected to occur and in many cases actually does occur. Any adsorption sheath, either of water or other molecules, would tend to prevent coalescence occurring on collision. The action of so-called "protective" colloids and, in certain cases, of crystalloidal non-electrolytes in preventing the formation of precipitates is explicable in this way.

That colloidal suspensions may be coagulated by the addition of electrolytes is well known, but the mechanism of the process is doubtful. It is supposed to occur and probably does occur in two stages, the neutralization of the charged particles followed by their coalescence. The neutralization is generally regarded as being due to the adsorption of that ion of the added electrolyte of opposite charge to the colloidal particle, and doubtless this is correct. It seems reasonable to look at the matter from the ordinary ionic point of view. The process may be akin to the throwing back of the ionization of an ordinary electrolyte by the mass influence of the added ion which is common to the two electrolytes. Neutralization might also be due to the electroaffinity of the ion which causes coagulation, being smaller than that of the simple ion split off from the colloidal complex and hence, also its tendency to remain ionized.[11]

Other things being equal, the efficiency of salts as coagulants might be expected to depend upon the electroaffinity of the anions in the case of positive sols and of the cations in the case of negative sols, and this may well be the basis of Schulze's law,[12] for in a general way electroaffinity falls off with increasing valency. The many exceptions to Schulze's law would also be explicable, for electroaffinity depends upon many other factors than valency.[13]

The matter is, however, complicated by adsorption of the un-ionized electrolyte and in many other ways, so that when different electrolytes are arranged in their order of effectiveness as coagulants, that order is not always easy to explain, while the amounts of the ions adsorbed are not even approximately equivalent.[14] *

Adsorption by the neutralized sol particles during their agglomeration seems to be one of the factors which most affects the relative amounts of different electrolytes carried down by the precipitate.[15] The high efficiency of acids as coagulants for negative colloids seems more satisfactorily accounted for by the low electroaffinity of the H. ion than by its high ionic conductivity and in fact most of Westgren's results [16] seem more intelligible when so explained. Thus the fact that, of the three sodium salts ($NaIO_3$, $NaCl$, $NaOH$) examined, the first is the most efficient coagulator for negative gold sols, and the third, the least, falls naturally into line with the fact that the IO_3' ion has the highest electroaffinity and the OH' ion the least. The IO_3' ion will most readily surrender its Nå ion to the negative colloidal particles, while the OH' ion will do so least readily.

In certain cases polyvalent ions may assist the process of coagulation in another way by actually linking together two or more of the colloidal ions.

The mutual precipitation of oppositely charged colloids can obviously be regarded as a special case of the process outlined above and in that sense is to be frankly regarded as ionic and chemical.

No simple stoichiometrical relationship is to be expected between the positive and negative constituents of the precipitates obtained by coagulating colloidal solutions, either by electrolytes or by other colloids, but this does not necessarily mean that the process is not chemical in the broader sense, and this is now being generally recognized. A good deal of experimental work is being directed towards the determination of formulæ for various sols which are regarded as highly complex salts.

Formulæ of the type of highly basic salts have been assigned to the sols of various metallic hydroxides by Pauli and others.[17] Metal sols contain particles which do not consist solely of the metal but which are complex and of a salt-like character.[18] The sol of arsenious sulphide is of the nature of a highly condensed sulph-arsenious acid.[19] The composition of the colloidal complexes (or micellæ) present in stannic acid or silicic acid sols has been investigated

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* See paper by H. J. Weiser, this volume, p. 600. J. A.

by Wintgren[20] and Pauli and Valko[20a] and their formulæ may be compared with those of McBain for the colloidal micellæ of soap solutions.*

That adsorption is often closely akin to ordinary chemical combination is shown by many facts and, among others, by the behavior of dyes towards various substrates. There is a recent paper by Rheinboldt and Wedekinn[21] which emphasizes this. It is shown that substrates of acidic character are only fast dyed by basic dyes and conversely. The behavior of dyes towards titanic acid and Stannic acid is in agreement with this.[22] Irreversible adsorption seems to be connected with more definite combination than occurs in ordinary reversible adsorption, but whether any sharp distinction can be drawn between the two types may be doubted.[22a]

Many of the phenomena observed in the adsorption of gases by partly or completely dehydrated zeolites suggest that it is not merely surface adsorption which occurs but that the gas or vapor actually enters into the crystal lattice in the position previously occupied by water.[23] In other words the adsorbed material is chemically combined just as much as was the original water.

After the particles in a colloidal suspension have been neutralized by ionic adsorption their coalescence or agglomeration follows more or less rapidly as a result of molecular collisions. The frequency of these depends mainly upon the concentration of the particles and their velocity, which again depends upon their mass and upon the temperature. The influence of these several factors has been considered in some detail by von Smoluchowski[24] and the equations he derives for the influence of the concentration of the colloid on the rate of coagulation are comparable with equations for ordinary chemical reactions of the second order. Sven Odén[25] has devised apparatus for automatically recording the rate of settling of precipitates and with its help has carried out important studies on precipitate formation.† He has tested von Smoluchowski's formula and found it satisfactory.[25a]

A great deal of work has, in fact, been carried out during the last few years to test von Smoluchowski's theory. Mukherjee and Papaconstantinou[26] found good support for it in their work on gold sols, while Lachs and Goldberg[27] found that the time required to coagulate gold sols at temperatures up to 70° by a constant amount of sodium chloride was inversely proportional to the absolute temperature as demanded by the theory. According to Kruyt and van Arkel[28] the theory is not capable of entirely explaining slow flocculation although there is a wide range, particularly for diluted sols, where it is verified.‡ The theory can be applied to borax fusions.[29] The variation in the precipitating value of various electrolytes with the concentration of the disperse phase has also been considered by Kruyt and van der Spek,[30] Burton and Bishop,[31] Weiser and Nicholas,[32] and Murphy and Matthews.[33] The behavior observed varies greatly with the valency of the ions concerned and depends to a large extent on the relative adsorbability of the precipitating ion and of the stabilizing ion. If the adsorption of the later is negligible and that of the former large, the precipitating value varies almost directly with the concentration of the colloid. This is found to be the case for tri- and quadri-valent ions.[34]

The influence of concentration of the colloid, shaking and temperature, on the flocculation of colloidal As_2S_3 varies with the nature of the electrolyte used to cause flocculation.[35]

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* See paper by J. W. McBain, this volume, p. 137. J. A.

† See paper by Sven Odén, this volume, p. 861. J. A.

‡ See paper by H. J. Kruyt, this volume, p. 306. J. A.

Mukherjee and Sen[36] have shown that increasing the distance between sol particles tends to stabilize the sol, so that, of two sols containing the same concentration of colloid, the one having finer particles is the more readily coagulated by electrolytes. The effect of temperature in altering the rate of coagulation of hydrosols by electrolytes seems to be largely due to modifications in the adsorbability of the different ions.[37]

Westgren and Reitstotter[38] have summarized Smoluchowski's kinetic hypothesis of coagulation and given an account of work which has been published with the object of testing it. More recent work on rate of coagulation has been published by Mukherjee and Majumba,[38a] Anderson,[38b] Freundlich and Basu,[38c] Jablczynski,[38d] and Paine and Evans.[38e] It is usually found that the results obtained in the region of rapid precipitation agree satisfactorily with Smoluchowski's theory but that there is only partial agreement in the region of slow precipitation. Other formulæ which more or less satisfactorily connect rate of coagulation and concentration of the precipitating electrolyte have been devised by Freundlich[38f] and by Schalek and Szegvari.[38g]

Sven Odén has considered the mode of formation of the secondary aggregates and their stability.[39] There seems no doubt that the adsorbed water (degree of hydration) plays a very important part at this stage and that coalescence of individual particles to form the secondary aggregates is largely due to capillary * forces between the particles coming into play. If these forces are small or the degree of hydration large, the secondary aggregates are not very stable and are easily broken down again—and this is in full agreement with the well established fact that lowering the interfacial tension between solid and liquid (or liquid and liquid) favors the formation of colloidal suspensions. If, however, the original degree of hydration is too slight (as with metallic particles), or if the aqueous envelopes surrounding the particles become broken, so that the particles come within the range of their cohesive * forces, then the secondary aggregates formed are much more stable and the transformation is not reversible. It is partly to enable such changes to occur in the secondary aggregates—changes which may sometimes amount to actual crystallization—that precipitates are frequently allowed to stand or even digested for some time before filtration.

The presence or absence of a water sheath on colloidal particles is largely dependent upon the chemical nature of the substance of which they are composed. With the so-called hydrophobic colloids the sheath appears to be more or less absent while it is considerable in the case of the hydrophilic colloids. The division of colloids into so-called suspensoids and emulsoids seems also to correspond in the main to a slight and to a large hydration respectively. The water sheath on the sol particles—or their degree of hydration which is another way of referring to the same thing—is of considerable importance as it introduces another stabilizing factor.

All colloids which readily "dissolve" in water and are capable of acting as "protective" colloids, as also all easily reversible colloids, appear to carry considerable water sheaths. According to Kruyt and de Jong[40] an emulsoid sol possesses two stabilizing factors: the electric charge on the particles and their hydration. Both of these must be removed before coagulation occurs. If the charge only is removed a lyophile sol remains, but if the hydration only is removed a suspensoid remains. Salting out is a combined discharge and dehydration. The action of alcohol, etc., in coagulating protected silver sols,[41] and indeed other sols, is no doubt mainly due to its dehydrating action.

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* On Langmuir's view of the matter (*loc. cit.*) these forces are essentially chemical.

It will be realized that in any individual case the formation of a precipitate may either be due to ordinary crystalline growth of the separating particles until they are sufficiently large to settle out, or the primary crystalline particles formed may be coagulated by the action of electrolytes present or by the action of oppositely charged particles, or a combination of these processes may even occur.*

It may not be easy to say which course is followed in any given case, but the more soluble a compound, the more likely is its precipitation to be due to simple crystalline growth and conversely.

It can, however, be asserted with confidence that, provided the precipitate is sufficiently insoluble, it will be the more desirable from the analyst's point of view the more its formation depends upon simple crystalline growth, owing to the greater readiness with which such a precipitate can be filtered and washed and to its greater purity.

It is evident that, as far as actual precipitation is concerned, all efforts should be concentrated on obtaining a crystalline precipitate or, if that is out of the question, an amorphous precipitate as dense as possible, that is to say one formed by coagulation of the largest possible colloidal particles. Precipitation must therefore be carried out as slowly as possible, and this is done by adding the precipitating solution very slowly, stirring all the time, to the other solution. Both solutions should be moderately dilute, the dilution permissible or necessary depending on the true solubility of the substance to be precipitated. Only a moderate excess of the precipitating solution should normally be employed owing to the danger of formation of crystalloidal complex salts and resolution of the precipitate, if large excesses of reagents are used. A very slight excess of precipitant may not be satisfactory as in such cases the slight excess may, with amorphous precipitates, cause peptization of the precipitate and formation of a colloidal solution as in the case of silver chloride (Lottermoser—*see* later).† A moderate excess of reagent is nearly always satisfactory as by its ionic effect it diminishes the solubility of crystalline precipitates and also helps the coagulation of amorphous ones—this being regarded above as also an ionic effect in reality.

Conditions should also be such as to ensure the greatest possible solubility (within reason, of course) of the precipitate at the actual time of its formation. An elevated temperature is generally favorable to this and in many cases proper attention to the acidity, etc., of the solutions may be very helpful. Once precipitation has been effected, the solubility is again lowered by allowing to cool and by complete or partial neutralization of any acidity, or possibly by other means. An elevated temperature may sometimes accelerate the electrolytic coagulation of sols which would be unfavorable to the formation of dense precipitates. A moderate temperature may therefore be better than either a lower or higher one for the precipitation of amorphous precipitates. This applies to aluminium hydroxide which is best precipitated at 66°.[42] Digestion subsequent to precipitation and even standing for some time at the ordinary temperature before filtration are also favorable owing to the opportunities so given for crystalline particles to grow at the expense of any very fine and more soluble ones that may be present or for amorphous precipitates to undergo those secondary changes which may amount to crystallization and which at least cause them to become denser.

Owing to the need for postponing the electrolytic coagulation as long as

* See paper of P. P. von Weimarn, this volume, p. 27. J. A.
† See also paper by A. Lottermoser, this volume, p. 670. J. A.

possible, attention must be paid to having as small a concentration of electrolytes present as is consistent with the general requirements of the experiment. The unfavorable effect of high salt concentrations on the character of precipitates is well known. The nature of the electrolytes present can also sometimes be controlled in the sense of ensuring the absence of those of very high coagulating power.

The need for precipitating substances as slowly as possible in analytical operations and with adequate mixing of reagent and solution is well known. A method of doing this which its author calls "Precipitation in extreme dilution," has been described by Hahn.[43] It consists in the slow simultaneous addition of the two reacting solutions to a small quantity of hot water. Very coarse and pure precipitates of even barium sulphate can be so obtained. The importance of vigorous stirring during precipitation has been pointed out by Dutoit and Grobet.[44]

Exposure to bright light increases the rate of coagulation of many colloidal solutions even when protective colloids are present.[45]* It seems probable that this is usually, if not always, the result of photochemical changes. These may lead either to the destruction of stabilizing electrolytes or to the production of others which act as coagulants.[46]

Filtration influences a sol in the sense of causing an increase in the size of particles. For this reason it tends to cause coagulation. Boiling also causes coagulation, probably as a consequence of an adsorption process at the liquid, vapor interface.[47]

There is an interesting condition of a sol which is intermediate between that ordinarily holding when the sol is at rest and the condition when coagulation or crystallization has occurred.

Many sols when in movement or when placed in a magnetic or an electric field show double refraction when examined between crossed nicols.[48] The properties of such sols are similar to those shown by crystalline liquids. The double refraction is probably due to formation of long particles produced by an ordered coagulation which is distinct from the usual un-ordered coagulation. Colloids such as gelatin or albumin in certain concentrations prevent the appearance of the double refraction; they act as protective colloids. Addition of electrolytes favors the production of this kind of double refraction and there is some similarity between the efficiency of different electrolytes in this respect and their efficiency as ordinary coagulants.[49]

That the precipitation of a colloid by an electrolyte is a complex phenomenon is now well recognized. In the simplest case the ion of the same sign as the sol particles tends to neutralize the precipitating action of the ion of opposite sign. When precipitation is produced by a mixed electrolyte conditions become still more complicated since the various ions of the same sign may modify each other's effects. If several electrolytes have approximately the same precipitating value, then for mixtures of these the effects produced are approximately additive. When the precipitating values differ widely, however, then in admixture the effects may be far from additive, relatively more of each electrolyte being required than if the others were absent.[50] The deviations from the additive relation depend also upon the degree of hydration of the colloid and are apparently not observed with definitely hydrophobic colloids.[51] A number of papers have been published recently which deal with the stabilizing effect of the ion of same sign as the sol particles.

* **See also paper by R. Audubert, this volume, p. 353. J. A.**

Many of these are of unnecessary length while there is much repetition and some contradiction.[51a]

From the analytical point of view the most important case of coagulation by mixed electrolytes is that in which it is brought about by positive ions in presence of hydrogen ions. A good deal of work has recently been done on this question.

Under otherwise comparable conditions different acids tend to precipitate negative colloids (*e.g.*, mastic) at the same p_H value. Only when the anion of the acid has a marked stabilizing effect on the colloid are marked deviations from this behavior to be noticed. The precipitating value of other cations depends on the p_H value of the solution and approaches a limiting value as this increases. For mastic sols the limiting values are reached when p_H is about 7 or 8.

The effects produced by different electrolytes in coagulating colloidal solutions should therefore be compared at the same p_H value and preferably at the limiting value.[52] * In the case of the flocculation of colloidal clay by a mixture of KOH and KCl it was found that the amount of electrolyte required for flocculation increased ten times when the p_H of the mixture increased from 6.2 to 8. Further increase in alkalinity was without effect.[53]

Purity, Filtration and Washing of Precipitates

In those cases where precipitation is due entirely to crystalline growth the purity of the precipitate will normally be of a high order.

Impurities are only present, in a form readily removable by washing, as a thin layer adsorbed on the surface of the particles. The coarser the precipitate the less its surface and the more readily can it be washed. As this form of precipitation is most likely to occur with compounds which are not highly insoluble, attention must be paid to the use of the minimum amount of wash-water.

Impurity of such precipitates, other than that which is due to surface adsorption and readily removable, is only to be feared in cases where isomorphous replacement is possible as, for example, in separating calcium, strontium and barium.

Crystalline precipitates, moreover, are not likely to pass into colloidal solution again during the process of washing, their passage back into solution being determined by ordinary solubility.

The above statements would, in some measure, apply also to the case of precipitates which have resulted from electrolytic coagulation of a sol, but where the secondary aggregates have undergone rearrangement, either to the extent of crystallization or, at least of a sufficient degree to cause rupture of the adsorbed water layers.

The case is very different, however, when the precipitate has separated wholly owing to electrolytic coagulation and without any subsequent rearrangement of the secondary aggregates. With this type of precipitate there is much more general surface adsorption because of the finer state of aggregation, but material so adsorbed is doubtless fairly readily removable by washing. One has in addition to deal with the much more intimately combined acidic or basic atoms or radicles which played such an important part in discharging the original charged sol particles or which had been taken up by them by the method of ionic interchange suggested previously. Atoms or radicles so attached will generally lie just on or in the surface of the constituent particles of the secondary aggregates composing the precipitate. Steric considerations will usually prevent their actual absorption into the crystalline particles unless there is possibility of some isomorphous replacement. The finer the sol particles are at the moment of coagulation the more serious is contamination of this kind likely to be, and, moreover, it cannot as a rule be removed by simple washing.

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* See also paper by L. Michaelis, this volume, p. 471. J. A.

The attachment of such contaminating groups or atoms has been attributed to ordinary chemical forces supported firstly by the mass effect (concentration) of the ion which becomes so attached, and secondly—especially in the case of polyvalent ions—by its relatively low electroaffinity. Which of these two factors is the more important will vary from case to case and the behavior of the precipitate on washing will largely depend upon which predominates. If the mass effect of the discharging ion is of much importance a relatively high concentration is required for the complete neutralization of the charged sol particles which must precede their coagulation. On washing the coagulum the mass effect is no longer sufficient, and although the contaminating radicle is thereby gradually removed, such removal is fatal to the continued existence of the precipitate. The radicle once more passes into the ionic state leaving its complementary particle in the precipitate charged and in a short time the precipitate disintegrates, the individual charged particles again passing into colloidal solution. Where the contaminating or discharging ion is mainly attached by virtue of its low electroaffinity such removal on washing is much slower and the precipitate does not so readily pass back again into colloidal solution.

Washing a precipitate with a solution of an electrolyte may be expected to counteract any such tendency to pass into colloidal solution and is indeed a well known analytical artifice. When the washing electrolyte is suitably chosen it may be possible to eliminate undesirable constituents from the precipitate almost completely and to obtain after ignition a product of the correct composition.

Some interchange between adsorbed material and material in solution will always occur. The tendency will always be for an ion which is readily adsorbed to replace one which is less strongly adsorbed. The following case, due to Charriov,[54] is of some analytical interest. Alumina precipitated by ammonia from a solution containing chromate is yellow owing to adsorbed chromate which cannot be removed by prolonged washing with boiling water, or with water containing ammonium nitrate, chloride or acetate. When, however, the alumina is precipitated with ammonium carbonate, instead of hydroxide, or if it is precipitated with the latter and subsequently washed with a 5 per cent solution of ammonium carbonate, it is obtained quite white and free from chromate. Carbonate ion has displaced chromate ion.

Generally it will not be possible to wash an amorphous precipitate entirely free from foreign radicles. As a consequence of this the weight, after drying or igniting the precipitate, may be what it should be from stoichiometric considerations, but it is much more likely to be slightly greater or even less, according to the nature of the foreign radicles in the precipitate. If the latter contains an element or group subsequently to be determined in the filtrate, the results obtained for it will be too low.

Analytical methods for estimating small quantities of soluble material present as impurities in insoluble substances which depend upon direct extraction with water must be looked upon with suspicion. The results obtained may be quite incorrect owing to obstinate retention of the soluble by the insoluble matter. It has recently been shown that alkalies present in precipitated calcium carbonate cannot be satisfactorily estimated in this way.[55]

The amount of any foreign radicles present in a precipitate depends very intimately on many factors, which makes the application of any empirical correction very uncertain even if great care is taken to carry out the precipitations always in the same way as far as possible.

The p_H value of the solution from which the precipitate separates is of great importance in determining the amount of adsorption which occurs. Aluminium hydroxide has been examined by Euler and Erikson [56] in regard to the amount of various substances it adsorbs or does not adsorb at various p_H values. This hydroxide has been used by Willstätter and Racke [57] * for adsorbing invertase and other enzymes for which purpose it has proved of great value. Its adsorptive capacity depends a great deal on the method by which it is prepared.[58]

The difficulty caused by marked adsorption of a readily adsorbed ion can sometimes be overcome by a modification of the adsorbent. Thus if phosphoric acid has to be determined after separation of tin a low result is obtained if the tin is removed as stannic sulphide owing to marked adsorption by the latter. Stannous sulphide, however, does not adsorb phosphoric acid appreciably so that if the tin is reduced by means of zinc and removed by stannous sulphide estimation of phosphoric acid in the filtrate gives correct results.[59] According to Anger and Odinot [59a] stannic sulphide carries down cobalt and nickel from a hydrochloric acid solution whereas stannous sulphide does not.

Now though the coagulating effect of an electrolyte has to be ascribed essentially to either the anion or the cation derived from it, it must be remembered that the other ion of same sign as the colloidal particles has a disturbing effect which may nullify or even reverse this coagulating effect. The first effect may well be neutralization of the colloidal particles, but before these have time to coalesce they become changed once more, but in the opposite sense either by direct adsorption of the opposite ion or by loss of its partner after preliminary adsorption of the un-ionized molecule.

From what has been said previously it should follow that this effect should be largely dependent upon the electroaffinity of the ion of same sign as the original sol particles, and it was actually found that in the case of negative gold sols NaOH was much the least efficient coagulator of the sodium salts tried and OH' was the anion of lowest electroaffinity.[60] The stabilizing effect of the strongly adsorbed H ion of low electroaffinity is also marked in the coagulation of positive ferric hydroxide sols.[61]

The stabilizing effect of the one ion of the electrolyte may come into action even after coagulation of the discharged sol particles and cause disintegration—peptization—of the precipitate and this occurs readily in the case of the hydrated colloids where secondary changes due to rupture of the water sheaths either do not occur or only very slowly. In such cases, too, it is also found that ions of low electroaffinity are frequently good peptizing agents. Thus alumina which is a positive colloid is readily peptized by acids.[62] Of course, the peptization also depends to some extent on the colloid and in some cases ions of high electroaffinity may be adsorbed as in the peptization of silver halides by the corresponding potassium halide owing to adsorption of the halogen ions.[63] The peptization of a gel, such as that of silver chloride,

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* See paper by R. Willstätter, Volume II of this series. J. A.

by a solution of KCl owing to adsorption of Cl′ ions, is so remarkably similar to the passage of a gel like silver cyanide into true solution in KCN owing to addition of CN′ ion that there seems no reason for doubting the complete analogy of the two processes. The negatively charged sol particles are to be regarded as complex ions in which the "neutral part" (in the terminology of Abegg and Bodländer, *loc. cit.*) consists, in this instance, of the original uncharged particle of silver chloride while in the crystalloidal cyanide solution the complex ion is $Ag(CN)^{\cdot}_2$ and its "neutral part" consists of a single molecule of AgCN. But the analogy goes even further, for under suitable conditions the colloidal solution of silver chloride in KCl passes into a crystalloidal solution containing the complex anion $AgCl_2'$ whilst weak solutions of KCN will peptize silver cyanide which forms a colloidal solution owing to adsorption of CN′ ions.[64]

In striking confirmation of these views is the fact that, corresponding to the colloidal solutions of silver halides in $Ag\ NO_3$ in which the sol particles are positively charged and owe their stability to adsorbed Ag ions, there are known definite crystalline compounds $Ag_2\ Cl\ NO_3$, etc., which ionize into complex *cations* $Ag_2\ Cl^{\cdot}$, etc.[65] It is probable that the passage into true solution of a gel under the influence of any electrolyte is, in all cases, preceded by a stage in which a colloidal solution is formed owing to adsorption of one or other ion. This certainly appears to occur when compounds such as aluminates and zincates are formed by the action of caustic alkalis on metallic hydroxides, and even when the latter dissolve in acids. Such transitions have recently been studied in an interesting manner in the case of silicic acid dissolving in ammonia,[66] and of titanic acid dissolving in hydrochloric acid.[66a]

According to Thomas and Frieden[67] the solution forces between the stabilizing agent and the solvent may be of as great or greater importance in keeping a colloid in the sol condition than the repulsive forces between the similarly charged particles. Thomas and Johnson[68] consider that the mutual precipitation of oppositely charged colloids is largely due to chemical interaction between their respective peptizing agents and the mutual destruction of these. In special cases this may occur but it would seem that, in the general case, maximum precipitation occurs when the concentration of the oppositely charged particles in "gram equivalent aggregates per litre" is the same.[68a]

In all cases of interaction between two different phases (solid and gas, solid and liquid, etc.) adsorption probably precedes (ordinary) chemical action. Thus, according to Schilov and co-workers,[69] when iron powder was kept in contact with a solution of silver nitrate, silver was removed from solution during the first 150 minutes to the extent of 3 to 8 per cent without iron passing into solution. Once the chemical action started, however, it proceeded very rapidly to completion.

Many organic colloids are peptizable by pure water, yielding sols containing either positively or negatively charged particles. Such colloids have a marked effect in preventing the coagulation of other colloids of similar sign to themselves and in that case are called "protective" colloids.* One can suppose that the one colloid is neutralized normally by the electrolyte added but is at once peptized by the water soluble colloid. That is to say the charged protective colloid particle is adsorbed by the neutral particles of the other colloid. Sen[69a] has emphasized the view that only ions or charged colloids can act as peptizing agents. Neutral molecules, such as sucrose, glycerol or egg albumin may effect a stabilization of sols by covering the colloid particles owing to adsorption, but this is only effective in presence of electrolytes. He considers that all cases of apparent peptisation by water are, in reality, cases of ion peptization.

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* See paper by J. Alexander, this volume, p. 619. J. A.

Such water-soluble colloids—and indeed other colloids too, though not in such a marked way—also have a great effect on the precipitation of many inorganic compounds. In the presence of protective colloids, compounds, which normally separate in coarse crystals, tend to separate in very minute crystals, while those normally separating in a fine state of division will separate in a flocculent condition and in extreme cases no separation at all occurs. These effects are all attributable to the formation in the solution of adsorption complexes, or complex ions, between the protective colloid and one or other of the ions of the compound being precipitated. This renders precipitation of the compound either impossible or at least difficult. It is well known that the presence of colloidal organic matter in solution is liable to give trouble in many inorganic estimations and that it should always be removed or destroyed if possible.

In this connection it should be remembered that colloidal electrolytes, such as soaps, have this protective action in a marked degree. The protective action of soaps was first noticed by Zsigmondy[70] and has been studied recently by Iredale.[71]

Colloid Properties of the Filter Paper, Surfaces of Vessels, etc.

Effects due to the colloid character of the filter paper (or indeed of other filtering materials) are sometimes not properly appreciated. The filter paper fibers are negative colloids, and when a precipitate which has resulted from the coagulation of a positive colloid is filtered through the paper, a sort of double decomposition occurs with attachment of the particles of the positive colloid to the negative filter paper. If the individual particles are sufficiently small this occurs in the pores of the paper, completely blocking them up and making filtration extremely slow. This sort of thing happens with aluminium hydroxide as usually precipitated, and with zinc sulphide when precipitated from alkaline solution and indeed is liable to happen with any similar positive colloid.[72]

Owing to their large surface, and their colloid character, the fibers readily adsorb dissolved substances from solution and also water. This adsorption is perhaps mainly due to the simple surface action, but it is partly of the more profound kind which occurs when a sol is neutralized by an electrolyte. It follows that a filter paper may not only remove soluble constituents from a solution being passed through it, but it may be extremely difficult to wash these out again. Errors can obviously be caused in this way. The weight of precipitate obtained after drying or ignition may be too great, while values found for constituents subsequently estimated in the filtrate may be too low. In extreme cases traces of substances may be entirely removed from solution by filter papers and so escape detection, though in suitable cases their removal by such means may be made the basis of a method for separating and estimating them. In cases where filter papers are used which are not of the ashless variety, disturbances may be caused by replacement of the inorganic constituents of the paper, which are probably present in the adsorbed condition, by other substances derived from the solution being filtered. The correction subsequently applied for the ash of the filter may then be wide of the mark.

Mainly on account of these adsorption effects the size of the filter paper used should always bear a reasonable proportion to the amount of precipitate being filtered. Adsorption of water by filter paper is troublesome in those cases where a precipitate cannot be ignited but has to be weighed on the filter. It is well known that the amount of moisture held by the paper varies considerably with the conditions, and that great care must be taken when working with weighed filter papers in order to get trustworthy results. Other filtering materials also show similar adsorption effects though to a differing extent.[72a]

It must be remembered that all surfaces, whether crystalline or amorphous, have some capacity for adsorbing substances either from solution or from the gaseous condition, and the aspect of this matter, which is of most importance to the analyst, is the adsorption of moisture from the air.

It may cause serious errors if suitable precautions are not taken and these are guarded against by such means as (1) never weighing substances in larger crucibles, glass vessels, etc., than are essential for the operation in hand, (2) where possible igniting substances or at least drying them at as high a temperature as possible before weighing, (3) keeping the atmosphere in which vessels are allowed to cool before weighing and that in which they are weighed, in as constant a condition as possible with respect to moisture by the use of desiccators and by having some drying agent in the balance case, (4) making the complementary weighings (*e.g.,* empty and full crucible) after as short a time interval as possible, (5) where extreme accuracy is needed a second vessel of similar size and weight is used as a counterpoise and similarly treated.

Except in the most refined work it is not as a rule difficult to eliminate the troubles due to this moisture adsorption, but there are a few notorious cases, such as those of ignited alumina and silica which readily retain and take up moisture, where special care is needed. In fact alumina, when suitably prepared and if it has not been heated above about 700°, is such a good absorbent for water vapor that it has been recommended as the best absorbent for use in organic combustions.[73] Adsorption of gases other than water vapour may cause difficulties in special cases, as in the analysis of fuels, according to Vondrácek and Hlavica.[73a]

It is probable that the tenacity with which some precipitates, especially sulphides and oxides, adhere to the sides of beakers, etc., in which they have been precipitated, is to be accounted for in terms of the mutual precipitation of two oppositely charged colloids—the glass in the cases mentioned acting as the negative colloid.

The origin of the charge on colloidal particles has been ascribed either to self-ionization or to ionization of adsorbed water or electrolytes. It is difficult * to imagine that self-ionization can occur with some substances such as carbon or gold which can be obtained in colloidal solution, and in such cases the charge must originate wholly from the ionization of adsorbed water or electrolytes or to ion-adsorption (which really amounts to the same thing). When such adsorbing material is in too massive a condition actually to form a colloidal suspension—*e.g.,* gold or silver foil or lumps of charcoal—this process of adsorption and ionization of electrolytes should lead to the simultaneous removal of cations and anions from solution in equivalent amounts and formation of a so-called electrical double layer since the ions liberated by the adsorbed electrolyte would have to remain in the immediate vicinity of the oppositely charged surface. Several studies of this type of process have been made recently.

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* On this question, see paper by I. Langmuir, this volume, p. 525. J. A.

Odén and Andersson[74], and Odén and Langelius[75] have shown that really pure charcoal adsorbs equivalent amounts of anion and cation from solutions of the nitrates of alkali and alkaline earth metals. Euler and Hedelius[76] obtained a similar result for the adsorption of $Ag\ NO_3$ and K Cl by very pure finely divided silver. Euler and Zimmerbund[77] have carried out similar experiments with finely divided gold and gold foil. In some cases, as for instance with salts of strong bases and weak acids in presence of charcoal or mineral oil as adsorbents, equivalent adsorption of cation and anion may apparently not occur even when the adsorbents are absolutely pure. This is because adsorption is accompanied by hydrolysis of the salt and preferential adsorption of the acid so formed.[78]

The adsorption effects noticed with ordinary impure adsorbents are frequently complicated by the impurities present. Thus with ordinary charcoal the ash constituents play an important rôle. The same also applies to filter paper. According to Kolthoff[79] the adsorption of acid by filter paper is almost entirely determined by the ash and due to chemical interaction between the acid and the mineral matter. Ash free paper or cotton wool hardly adsorb any acid. Indeed from the experiments of Masters[80] the tendency seems to be for it to adsorb the base from neutral salts and leave the acid.

In a somewhat similar way the adsorption effects observed with glass wool seem to be largely determined by the alkaline character of this material.[81] Asbestos which has been carefully purified by treatment with acid practically does not adsorb positive ions whereas ordinary impure asbestos does and cannot safely be used as a filtering medium.[82]

Probably in many other cases ion adsorption is very largely a process in which a sparingly soluble substance contained in the adsorbent (or one strongly adsorbed by it) is converted by the adsorbed ion into another sparingly soluble substance.[83] Kolthoff[84] has shown that, though ash free filter paper and asbestos purified by acid do not adsorb appreciable quantities of lead, its adsorption by impure asbestos or filter paper of high ash content can be applied to the estimation of lead in drinking water. The solution in which lead is to be estimated is treated with a solution of sodium hydroxide containing carbonate. Most of the lead is precipitated and the rest adsorbed during the filtration. It is subsequently removed from the filtering medium for colorimetric or other estimation by treatment with acetic acid. According to Kolthoff[85] the ash of the filter paper functions as a permutite in which the bivalent cation may be replaced by hydrion or a heavy metal ion. Bases with a dissociation constant of not less than 5×10^{-9} can be removed almost completely from neutral solution by "permutite" which has been suggested as a reagent for amines,[86] and ammonia.[86a] Base exchange is only a special case of ion exchange which plays such an important part in adsorption phenomena.[86b]

The adsorption of base and not of acid from solutions of neutral salts by pure silica is, according to Joseph and Hancock,[87] essentially a chemical process and due to the formation of complex silicates of low solubility, although this view is not accepted by Mukherjee.[87a]

[Some color changes consequent upon adsorption are described in a paper by Hsien Wu and Daisy Yen Wu, this volume, p. 380. J. A.]

THE SURFACE AREA OF ADSORBING MATERIAL AND THE THICKNESS OF THE ADSORBED LAYER

As a knowledge of these matters is of considerable analytical interest they are briefly referred to here.

A rapid and trustworthy method for determining the surface area of an adsorbing powder in special cases has been described by Paneth and Vorwerk.[88] It is a radioactive method in which the distribution of an isotope of the metal present in the adsorbing powder between powder and solution is determined. In this way the surface area of lead sulphate was determined by means of thorium B.

A knowledge of the surface area of the adsorbent enables one to calculate the thickness of the layer of adsorbed material. Paneth and Vorwerk [89] have shown that when ponceau-2R is adsorbed by lead sulphate the adsorbed layer is one molecule thick. Radioactive methods are undoubtedly of great value for the study of adsorption and studies of this character by Brown,[90] Cranston and Burnett,[91] and Cranston and Hutton [92] may be referred to.

The adsorption of silver ion by gold and silver foil gave Euler and Rudberg [93] results which would correspond to an adsorption layer more than one molecule thick but which are probably to be interpreted as indicating roughness of the foil surface. On this assumption their results give a measure of this roughness. It would appear that, in the case of at least some emulsions, a layer of the adsorbed material of not more than unimolecular thickness is formed round the droplets and that if there is not sufficient of the substance being adsorbed to produce such a layer the emulsion is not stable.[94]

According to Langmuir [95] all adsorption is chemical in character and should lead to the formation of an adsorption film not more than one molecule thick. He showed [96] that unimolecular adsorption layers were actually formed when various gases were adsorbed by plane surfaces of glass, mica or platinum. Carver [97] finds that at 0° the adsorption of toluene vapor by a plane glass surface is generally in agreement with Langmuir's views. There seems no doubt, however, that when easily liquefiable gases such as CO_2 or NH_3 are adsorbed by such substances as glass fibers the adsorbed layer may be much more than one molecule thick unless the gas pressure is exceedingly low.[98] McHaffie and Lenher [98a] have shown, not only that the adsorption layer may be many molecules thick, but that, for each temperature, there is a definite equilibrium pressure corresponding to each thickness of the layer.

Wo. Ostwald and Izaguirre [99] maintain that an adsorption layer need not be of unimolecular thickness as a maximum. For the adsorption of colloid particles the layer must be at least *uni-micellar*. The same authors [100] consider that adsorption is always that of a *solution* of the solute—not simply of the solute.*

CONSIDERATION OF A FEW SELECTED ANALYTICAL METHODS

Estimation of lead sulphate.—Owing to the relatively high solubility of $PbSO_4$ its precipitation is probably entirely due to crystalline growth. The solubility is lowered by addition of sufficient sulphuric acid for the full mass effect of the SO_4'' ion to come into play and by washing the precipitate with dilute sulphuric acid followed by dilute alcohol.

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* For evidence of the common occurrence of polymolecular layers see *e.g.*, paper by W. D. Harkins, this volume, p. 192. J. A.

Separation of calcium as oxalate.—Calcium oxalate has a very small solubility product and when precipitated from ammoniacal solutions, as frequently recommended, often gives trouble by running through the filter paper. This is because it has separated under conditions of great insolubility and probably by coagulation of a finely divided sol. The C_2O_4'' ion is very sensitive to hydrogen ions and readily yields the HC_2O_4' ion, calcium oxalate therefore readily dissolves in dilute acids and even in water dissolves more than might be expected owing to the $H^{\cdot}$ ions present in water.

If therefore the precipitation is carried out in weak acid solution, the solution being made ammoniacal at the end of the precipitation, the precipitate forms much more slowly and probably entirely owing to crystalline growth and no trouble is experienced with the filtration. The precipitate is best washed with 2·5 per cent ammonia. When the method of Jarvinen [101] is used glittering crystals of calcium oxalate are obtained.

Precipitation of barium sulphate.—It seems likely that barium sulphate represents a border line case, and that by very carefully regulated slow precipitation from hot solutions, the forces of crystallization are just sufficient to cause precipitation independently of electrolytic coagulation. As a rule, perhaps, the precipitate results from such coagulation, but even then there is a marked tendency for the precipitate to undergo secondary changes and become denser, either on digestion with the mother liquor, or on standing. These secondary changes are not necessarily profound enough to eliminate troubles due to adsorption which may be very serious. The precipitation of barium sulphate has been very carefully examined largely on account of its importance in connection with the estimation of sulphur in iron pyrites. An interesting account of this work is to be found in Classen's *Ausgewählte Methoden der analytischen Chemie.*, 1903, Vol. II., pp. 305-318. Heavy metals and various acid radicles are readily carried down by the barium sulphate, the most important cases practically being those of ferric iron and chlorine. Colloidal solutions of barium sulphate are usually positive due to strong preferential adsorption of $Ba^{\cdot\cdot}$ ions; and all the experimental evidence supports the view that other metals are carried down owing to combination of negative complexions such as KSO_4' or $Fe_2(SO_4)_4''$ with the positive particles of the barium sulphate sol.[101a] When this occurs low results are obtained for SO_4. High results for SO_4 are, however, obtained when chlorine or similar ions are removed from solution by the barium sulphate. In so far as Cl' ion has combined with a sol particle owing its positive charge to $Ba^{\cdot\cdot}$ ions it is quite correct to say, as is generally done, that the precipitated barium sulphate has carried down barium chloride. The explanation of these processes given by Kolthoff and Vogelensang [102] is really identical with the above though at first sight rather different.

Slow precipitation from hot dilute solution goes a long way towards ensuring a pure precipitate, but in presence of ferric iron and similar metals, the only safe mode of procedure is to separate the metal first as in Lunge's well known method for iron,[103] or the modification proposed by Kuster and Thiel.[104]

Moderate acidity is beneficial in minimizing the adsorption of heavy metals by barium sulphate.

The estimation of barium is less troublesome than that of sulphate though both are precipitated as barium sulphate. The excess of sulphuric acid present in the one case renders adsorption of ions other than SO_4'', more difficult.

Metallic hydroxide precipitates.—All those of importance as a means of separating and estimating a metal are very insoluble and hence, are "amorphous," being formed as a result of electrolytic coagulation. The water they contain is much more vaguely and loosely held than that present in crystalline hydrates, and often regarded as held merely by adsorption. At the same time there are strong reasons for regarding these substances as hydroxides. The case of copper hydroxide is interesting. Copper is sometimes precipitated as that compound, but under the conditions of the usual analytical procedure dehydration of the sol occurs simultaneously with or shortly after its coagulation, with formation of what is essentially copper oxide. After thorough washing and ignition, the weight of oxide obtained is generally only very slightly higher than the theoretical. According to Kohlschütter & Tüscher [105] the elimination of water from copper hydroxide is due to amphoteric ionization and neutralization of molecular complexes of colloidal dimensions. This apparently indicates that the hydroxide in its acidic and basic forms, acts as its own coagulator, and so has little tendency to be coagulated by and adsorb foreign ions. If dehydration occurs subsequent to coagulation any foreign radicles present would probably be expelled at the same time. In certain cases marked adsorption may occur however. A good quantitative separation of copper and zinc, for instance, cannot be obtained by precipitation with excess of caustic soda or potash. Although the bulk of the zinc hydroxide dissolves in the excess, the copper oxide always retains a little, owing no doubt to its having taken part in the above indicated amphoteric neutralization of the copper hydroxide. Other similar well known cases of separations which are unsatisfactory quantitatively but work well enough qualitatively may possibly be explicable in a similar way. Such cases are the separation of ferric iron from aluminium with excess of caustic soda and the separation of ferric iron by means of ammonium hydrate in presence of ammonium salts from manganese, zinc, nickel or cobalt. In some of these cases atmospheric oxidation plays a part.[106]

It should be mentioned, however, that according to Lundell and Knowles [107] moderate amounts of iron or aluminium can be separated from manganese or nickel by means of ammonium hydroxide as satisfactorily as by the basic acetate or barium carbonate processes. All that is necessary is that sufficient ammonium chloride should be present, that only enough ammonia is added to give a p_H value of 6.5 to 7.5 and that the alkaline solution is not boiled for more than one or two minutes. Luff [108] has also studied the separation of iron and aluminium from the metals of analytical group IV by means of ammonia or pyridine. Under specified conditions one precipitation gives a satisfactory separation from manganese, but several reprecipitations are needed with the other metals. The amount of the contaminating oxide which is carried down by an hydroxide precipitate depends, as was to be expected upon the relative proportions in which the two metals are originally present in solution. Toyokichi Yasni [109] found that when the solution contained Cr_2O_3 and ZnO in the ratio 1 : 11 the weight of ZnO found in the precipitate might be one and a half times that of the Cr_2O_3. Toporescu [110] states that the amount of CaO or MgO carried down by chromic hydroxide increases with the concentration of calcium or magnesium salt present. It approaches a limit corresponding to chromites $Cr_2O_3 . 3CaO$ or $Cr_2O_3 . 3MgO$. He says that the whole of the CaO can be removed by washing the precipitate on the filter with boiling 5 per cent solution of ammonium nitrate, while MgO is best removed by washing by decantation with the same solution.

To get the minimum co-precipitation of lime with ferric hydroxide the concentration of calcium salt should be as small as possible and the minimum amount of ammonia should be used.[111]

The nature of the precipitating medium is also of some importance. Thus Scheringa[112] found that ferric hydroxide always carried down zinc when precipitated by caustic soda—even if the zinc salt be added after the caustic soda. Precipitation with cold 25 per cent ammonia solution gave a complete separation, however, if ammonia of the same strength was used to wash the precipitate.

The well-known fact that many hydroxide precipitates gradually become less reactive, and less readily soluble in acids, may well be due in part to some such process as that outlined for copper hydroxide, though not proceeding to such a degree of dehydration as in that case. There seems little doubt at any rate that it is connected with some loss of water either from the sol particles or from the gel.

A similar change seems to be the cause of the instability of the solutions of many hydroxides (*e.g.*, that of aluminium) in caustic soda, or in ammonia (*e.g.*, chromium hydroxide) or even in acids (*e.g.*, the slow hydrolysis of ferric chloride solutions) although the type of crystalloidal compound initially present in the solution is quite different in the three cases. If the concentration and proportion of caustic alkali, ammonia or acid are not excessive, the metallic hydroxide molecules formed by hydrolysis gradually unite to form highly disperse sol particles which in time coalesce, undergo some dehydration, and ultimately separate in a relatively dense and unreactive condition. According to Fricke and Windhausen[112a] no dehydration occurs but only an increase in the size of particles when chromium hydroxide separates from caustic potash solutions.

Gradual loss of water accompanied by decreased reactivity and decreased tendency to revert to the sol condition is shown by practically all inorganic colloids and is much accelerated and intensified by desiccation. Use is sometimes made of this fact during analysis as, for instance, in the estimation of silica which is always evaporated to dryness before filtration so that it may become less soluble (colloidally and otherwise). The phenomena observed are somewhat complex and have been studied especially by van Bemmelen. His work on silicic acid is to be found in *Z. anorg Chem.*, 1896, 13, 233-356.

The optimum condition of acidity for the complete precipitation of aluminium by ammonia has been studied by Blum,[113] who states that $[H^{\cdot}]$ should be between $10^{-6.5}$ and $10^{-7.5}$.

Owing to the very insoluble nature of the amorphous hydroxides it is not so easy, as in the case of crystalline precipitates, to precipitate them sufficiently slowly to markedly improve their mechanical properties. Sometimes this can be done, however, as in a method for iron, recently described,[114] which gives a dense powdery precipitate of ferric hydroxide which is easily filtered and washed and which is of a high order of purity. The reactions involved are

$$2Fe^{\cdot\cdot\cdot} + 2S_2O_3'' \rightarrow 2Fe^{\cdot\cdot} + S_4O_6''; \; 2Fe^{\cdot\cdot} + 6H_2O + IO_6' + 4S_2O_3'' \\ \rightarrow 2Fe(OH)_3 + I' + 2S_4O_6''.$$

The ferric solution is neutralized so far as possible and then warmed with thiosulphate solution until practically colorless. It is then warmed with twice the theoretical quantity of thiosulphate and a slight excess of iodate as calculated from the second of the above equations. The volume of solution should be about 400 c.c. per 0.2 grm. Fe_2O_3. It is sufficient to warm it on the water bath but the precipitate should be ignited over the blowpipe.

A detailed study of various hydrous oxides has been made of recent years by several workers with a view to determine whether there was any clear evidence for the existence of definite hydrates. The evidence is very conflicting so far as the precipitated oxides are concerned. Thus Weiser[115] found no indications of definite hydrates in the precipitated hydrous ferric or aluminium oxides, although one definite hydrated oxide both of iron and aluminium, prepared by special methods, is known.

He considers that what differences are found between different preparations are entirely due to differences in size and hydration (in the adsorption sense) of the constituent particles. He finds the same for hydrous chromic oxide[116] and cupric[117] oxide. Willstätter[118] and several recent writers, on the other hand, consider that the differences found between hydrous aluminium and other oxides prepared by various methods indicate that the preparations do not differ merely in the dispersivity of the hydrogel. Different hydrates appear to be involved in some way. After investigating hydrous cupric oxide by several methods, Losana[119] draws conclusions which seem unlikely to be correct. He thinks that the existence of no less than five definite hydrates of cupric oxide has been proved, as well as their formulæ. Tower[119a] concludes that nickel hydroxide, as ordinarily precipitated, really contains $Ni(OH)_2$.

Several hydrous acidic oxides have also been examined recently. Hürtig and Kurse[120] found that, on gradually dehydrating the tungstic acids, the time-composition curve indicated the existence of a definite hydrate . $WO_3 . H_2O$ in the case of the yellow acid, while the white acid only gave a smooth adsorption curve. Both Weiser[121] and Collins and Wood[122] agree that the differences between the various stannic acids are essentially due to variations in dispersivity and in content of adsorbed water but Willstätter and others[122a] maintain that this is not so and that several definite hydrates exist both in the case of stannic and silicic acids. Wood[123] could obtain no clear evidence for the existence of definite hydrates of antimonious oxide. This appeared to be largely due to the readiness with which amphoteric neutralization of acidic and basic forms occurred with consequent elimination of water and formation of the anhydrous oxide.

On the whole it may be said that recent physico-chemical work on the hydrous oxides extends and confirms the early work of van Bemmelen[124] and supports his view that the water in these substances is held essentially by adsorption.

At the same time it must be remembered that they show several peculiarities of behavior on dehydration which are not altogether easy to account for. It may even be doubted whether a consideration of the dehydration curves, or of any other test so far tried, enables a fair decision to be made as to whether definite hydrates are present or not in the case of hydrogels where the degree of dispersivity is relatively high. Even if there were a definite hydrate in any given case the pressure of water vapor in equilibrium with it would be higher the smaller the particle. If the hydrogel contained particles of many different sizes, as it might well do, its dehydration curve would contain so many small breaks that it would appear as a smooth continuous curve—an adsorption curve. The hydrous oxides, both basic and acidic, behave in so many ways as though they contained hydroxyl groups that even in cases where we cannot isolate definite hydrates owing to complications due to adsorption we should keep an open mind as to the possible existence of definite hydrates nevertheless. It must never be forgotten that the colloidal state (both the "sol" and "gel" condition) is a special intermediate state of matter where ordinary chemical forces are more or less obscured by surface phenomena. This intermediate colloidal state may be passed through with greater or less rapidity whenever a solid passes into crystalloidal solution or conversely. Failure to realize these facts leads people to attempt to explain many phenomena either in terms of definite compounds or on a purely colloidal basis in spite of evidence pointing the other way. Which explanation is nearer the truth may sometimes be a question of the experimental conditions being considered. Many attempts have been made to explain the solubility of heavy metal hydroxides in caustic alkali solutions in terms of colloidal suspensions. Under certain conditions the colloidal explanation is probably correct. It will depend upon the concentration of the alkali, among other things. Doubtless the statement of Chatterji and Dhar [125] that the major portion of the hydroxides of Al, Cr, Pb, Hg and Cu in NaOH or KOH solutions exists as colloid is correct in certain cases. So also, in all probability, is that of Creighton [126] that none of the blue solutions of cupric hydroxide in alkali exhibit the characteristic properties of colloidal solutions, the indications being that cuprates are formed. In any case the work of Müller and co-workers [127] on the system CuO — NaOH — H_2O has shown that a definite sodium cuprate can actually be crystallized from aqueous solution.

Dhar and Sen [128] want to explain all alkaline blue cupric solutions in terms of peptized negatively charged cupric hydroxide, while Sen and Dhar [129] attribute the non-precipitation of the hydroxides of Fe, Hg, Co, Cu, Ni, Mn, Cd, Th and Ce by alkali hydroxide in presence of various carbohydrates such as sucrose, dextrose, starch or glycerol entirely to colloidal effects (peptization).

The age of the solution, especially when the concentration of alkali is relatively small, is of great importance. Owing to hydrolysis there will be a tendency for cuprates and similar compounds to slowly decompose and give a colloidal suspension of a denser form of the hydroxide than was originally dissolved as has already been pointed out above.

The sulphides of analytical groups II and IV present several features which recall those found among hydroxide precipitates. They are so insoluble that their precipitation is essentially a colloidal process and they adsorb large quantities of water. This tends to result in bulky gels built up of aggregates of very small particles. The water content of the precipitates is variable and loosely held, which accounts for the difference in views as to whether they are hydrated sulphides or hydrosulphides or even partly hydroxides and hydrosulphides. Possibly all these compounds may be present in different cases and under different circumstances. The tendency to lose water—and perhaps H_2S too—seems to be even more marked among the sulphides than among the hydroxides, and with this is connected the remarkable difficulty with which the sulphides of cobalt, nickel and, to a less extent, zinc and other metals dissolve in acids although very little acid will prevent their formation in the first instance. Amphoteric neutralization similar to that discussed in the case of the hydroxides may well take place with the sulphides too and be partly responsible for the readiness with which some of the group II sulphides, notably that of copper, carry down from acid solution sulphides of group IV metals such as zinc.

This view is not necessarily opposed to the statement of Kolthoff and van Dijk [130] that the carrying down of zinc by cupric sulphide is a time phenomenon and that if the cupric sulphide is precipitated rapidly it carries down less zinc than when it is precipitated slowly.

It is to be noted that zinc sulphide occupies much the same position among the sulphides as aluminium hydroxide among the hydroxides, with regard to the trouble it gives in filtering and washing. The reason is likewise that the individual particles of the gel are ordinarily very small and highly hydrated. The trouble can be overcome by precipitation from slightly acid solutions when the slightly greater solubility permits the formation of a coarser, denser, precipitate. The acidity must not be too great, otherwise precipitation would be incomplete. These difficulties have been overcome in several ways, as for instance in the very good method of Riban [131] where the precipitation is effected from a dithionic acid solution. According to Fales and Ware [132] $[H\cdot]$ should be between 10^{-2} and 10^{-3} for the formation of a satisfactory precipitate.

Bornemann [133] states that the precipitation of zinc sulphide in a dense form is greatly facilitated by co-precipitation with another colloid, especially sulphur. This is carried out by passing a brisk current of H_2S through an acetic or chloracetic acid solution in presence of $NaHSO_3$. The dense precipitate obtained is washed on the filter with $0{\cdot}5 - 1{\cdot}0\%$ NH_4NO_3.

Perhaps it need scarcely be mentioned that just as many hydroxides and sulphides gradually become less readily soluble and less reactive in course of time, so also does their tendency to be readily peptized diminish. The tendency of some sulphide precipitates to pass through the filter paper during washing which is usually ascribed to atmospheric oxidation and is prevented by washing with H_2S water seems to be partly a colloidal phenomenon and can be largely prevented by the use of ammonium nitrate instead of H_2S—which is of course also a weak electrolyte.

It must be remembered that dissolved hydrogen sulphide has a marked stabilizing effect on pure sulphide sols both in aqueous and non-aqueous media.[134] In the presence of electrolytes this protective action is not always observed.[135] Thus hydrogen sulphide renders arsenious or mercuric sulphide sols more stable against coagulation by salts of univalent cations but less stable towards salts of cations of higher valency. Cupric sulphide sols on the other hand are more easily coagulated by salts in presence of H_2S no matter what the valency of the cation. Solutions of alkali sulphides tend to stabilize all three of the above mentioned sulphides against precipitation by salts of mono-, di-, or tri-valent cations but as alkali hydroxides do the same the effect may be mainly due to the hydroxyl ions present owing to hydrolysis.

When arsenic is estimated as As_2S_3 after precipitation with H_2S it is usual to remove the excess of H_2S by a current of CO_2 before filtration. This is done partly to eliminate possible trouble owing to the above mentioned tendency for H_2S to cause retention of As_2S_3 in the sol condition.

SEPARATION AND ESTIMATION OF SOME ORGANIC COLLOIDS

Organic colloids as a rule are not so readily precipitated from solution as are inorganic sols. Their estimation has frequently great biochemical and technical importance and methods are used for precipitating them which are similar to those used for coagulating inorganic sols. Precipitation by means of electrolytes or by a colloid of opposite sign are almost invariably used. Probably a majority of chemists are now satisfied that many, if not all, of these precipitations are essentially chemical in nature, although the precipitates formed lack that definitiveness of composition characteristic of classical chemical compounds.

Tannin.—This in solution carries a negative charge and is practically always estimated by some method involving precipitation by means of a colloid of opposite sign. The standard method is to adsorb the tannin under certain specified conditions by means of hide powder. After Procter's work on the subject there can be little doubt that real chemical combination occurs between the tannin and the hide powder. Other positive colloids have also been used in place of hide powder, such as:—fat-free casein,[136] nickel hydroxide,[137] aluminium hydroxide.[138]

The acidity of the solution is of great importance for the mutual precipitation of tannin by gelatin [139] or by hide substance.[140] For gallotannic acid the optimum acidity corresponds to p_H 4.4 — 4.6 but there is a definite optimum p_H value for each sort of tannin and if the acidity is not adjusted to near this value a precipitate may fail to form. Under the optimum conditions tannin can be detected by means of gelatin at dilutions as high as 1 in 100,000 to 200,000. Gelatin can be completely precipitated by tannin under the optimum conditions when the ratio of tannin to gelatin is not less than 2 : 1.

Proteins and related compounds.—The estimation of these is of fundamental importance for physiological and pathological chemistry, but is also of great difficulty. Some of these bodies (*e.g.,* albumin) are coagulated by heat, others by this reagent and others by that. The difficulty, however, is that such differences as exist are none too sharp, since the chemical gradation of the compounds in question is too gradual. Moreover, the presence of one compound may lead to the co-precipitation of another under conditions where it would not have been precipitated if present alone. Such behavior recalls the similar cases discussed when dealing with the precipitation of metallic hydroxides and sulphides. In spite of the difficulties the analytical knowledge of the proteins and similar bodies is far advanced as the result of much laborious work. Precipitation of protein, etc., can be effected by means of other colloids such as dialyzed ferric hydroxide (Michaelis and Rona) or aluminium hydroxide jelly,[141] while basic lead acetate should probably come in this class also. Owing to the amphoteric nature of the proteins it is probable that precipitation can be brought about by either positive or negative colloids under suitable conditions. These colloidal precipitants are not very discriminating, however, and where it is necessary to separate various classes of proteins and related compounds, the precipitation is generally affected by means of electrolytes. Temperature and concentration are of course important as in all such cases. So many precipitating re-agents have been recommended for this or that substance that it is hard to know which is best. Most acids can be used, and many have been, from the common inorganic ones, or others like phosphotungstic acid, to organic ones such as trichloracetic or sulphosalicylic. Various neutral salts may also be employed either ordinary ones such as $(NH_4)_2SO_4$ or $CaCl_2$, or less common ones such as uranium acetate.

In some cases the precipitating action appears to be specific, but in most cases various proteins may be precipitated by the same reagent, although a different concentration and temperature may be required in each case. Whether the mechanism of the coagulation is the same in all cases may be doubted, for several causes may be operative. A comparatively high concentration of the precipitant is often required, so it may well be that, in the formation of the coagulum, neutralization of the charged sol particles and their coalescence, is followed by dehydration of the gel, as discussed by Procter in connection with gelatine.[142] Considerable amounts of the precipitating agent are carried down by the coagulum in many cases, and are difficult to remove by washing. As some proteins are soluble in (peptized by) salt solutions, and others readily soluble in acids, the actual technique of protein separations and estimations becomes very troublesome. A paper by Cullen and van Slyke [143] may be referred to to illustrate the methods used when dealing with a complex substance like blood plasma.

The hydrogen ion concentration plays a very important part in all work with proteins. Attention has been drawn to this recently by Bogue,[144] who shows that salt precipitations of gelatin should be made at a hydrogen ion concentration corresponding to the isoelectric point if the maximum precipitation is to be obtained. The conditions of acidity under which precipitations of protein are effected are of course important in blood analyses.[145]

The various coagula obtained by precipitating proteins with different reagents may adsorb non-colloidal compounds which have to be subsequently estimated in the filtrate. The extent and nature of this adsorption may depend on the method or reagent used for precipitating the proteins. Examination of protein precipitation from this point of view is therefore of some importance. Some work of this character has already been published.[146]

Alkaloids.—There is a good deal of similarity between the precipitation of alkaloids by some of the general alkaloidal reagents and the precipitation of proteins by the same reagents. According to Heiduschka and Wolf [147] the precipitates obtained with silicotungstic acid and dilute solutions of alkaloids are colloidal in character. On addition of electrolytes or, in some cases, on standing, flocculation occurs and the precipitates can be filtered. Under specified conditions these precipitates appear to correspond to one of two distinct and definite types of compound according to the alkaloid concerned, though with other alkaloids the compounds are more complex and less definite.

Phosphotungstic acid behaves in a similar way. In cases where the precipitates are only slightly altered by washing with 0.1 per cent sodium chloride solution the alkaloids can, in the absence of protein, be estimated by titrating with NaOH the silicotungstic acid left in the filtrate.

Starch can be quantitatively precipitated by means of iodine.[148] The sensitiveness of the starch iodine reaction has been examined recently by Kolthoff.[149] It is well known that not only starch and iodine but also salts, especially KI, are involved in the formation of the blue substance.[150] The precise mechanism of the reaction is still obscure, but it would appear that the negatively charged starch particles first take up positive ions, and that the aggregates so formed adsorb iodine.[151]

However, Euler and Myrbäck [152] have come to the conclusion that starch alone can take up iodine in absence of iodide or other electrolytes (other than any which may be present adsorbed in the starch). They consider that there is evidence for the formation of two definite compounds of starch and iodine. Experiments by Firth and Watson [153] confirm the fact that iodide is not necessary for the formation of the blue starch iodine complex but they also show that the sensitiveness of the reaction is greatly increased by the presence of iodide. A starch solution containing 4 grms. starch and 0.348 grm. KI per litre will detect iodine in N/20000 solution. It is highly probable than under ordinary analytical conditions both iodine and iodide ions (or I_3' ions) are involved in the reaction. Mylius [154] showed that the blue precipitate, obtained by adding starch to a solution of iodine and hydriodic acid containing sulphuric acid, contained both iodine and hydriodic acid. When iodine alone is added to starch sufficient iodide ions are formed by hydrolysis and reduction (by the starch) to account for adsorption of iodine and formation of the blue complex.[154a]

MISCELLANEOUS

Use of colored adsorption products as indicators of the end point in titrations.—The blue starch-iodine complex is an example of this type of indicator. Other interesting examples have been described by Fajans and Hassel,[155] who found that silver halide sols cause characteristic color changes in very weak solutions of the alkali salts of fluorescein and its halogen substitution products when excess of silver ion is present. So long as halogen ions are present in the solution particles of silver halides tend to be negatively charged owing to adsorption of halogen ions. When more silver ion has been added than is required to combine with all the halogen ion, reversal of sign of the silver halide particles occurs owing to adsorption of silver ion. The positive sol particles so formed then adsorb the dye anion. This causes a color change, which under appropriate conditions may be sharp enough to show correctly the end point of the titration. Chlorides can be so titrated in presence of fluorescein, the concentration of which should be about $\frac{1}{300000}$ molar. A reddish color shows the end point in this case. $\frac{1}{30000}$ molar eosin can serve as an indicator in the titration of iodides, the end point being shown by the appearance of a violet color. In a mixture of iodide and chloride, titration in presence of eosin will give the iodide alone, while the sum of the two halogen ions can be obtained with fluorescein as indicator.

Colloidal matter in soils.—The study of the colloids present in soils plays an increasing part in agricultural analysis. Many attempts have been made to estimate the amount of the amorphous or colloidal matter present by determinations of the adsorptive power of the soils for certain dyes. It is not as a rule a question of any absolute determinations being possible, but comparative results of a kind can be obtained, though possible disturbing effects on the dyes themselves by traces of electrolytes present must be borne in mind, as pointed out by Oryng.[156]

A method for determining the colloidal matter present in soils, which are more or less free from organic matter, has been developed by Moore, Fry and Middleton,[157] which gives approximately absolute values. After shaking the soil with water, settling and centrifuging, the resulting opalescent liquid was filtered through Pasteur-Chamberland tubes. The "ultra clay" collected on the tubes was washed and dried at 110° and consisted essentially of hydrated aluminium silicate. By comparing the amount of dry NH_3 adsorbed by the dried "ultra clay" with that adsorbed by the soil the percentage of "ultra clay" present in the soil was obtained. The result so obtained was similar to that deduced from a comparison of the amounts of malachite green adsorbed from ammonium oxalate solution by the "ultra clay" and soil respectively. The acidity in soils appears to be largely associated with the colloidal clay fraction.[157a]

Attempts to distinguish so-called soluble or amorphous silica from other forms have long been made in soil and clay analyses and many different solutions and methods have been put forward for the purpose. They all give different results, however, and none of them are trustworthy.[158] The fact of the matter is that most soils and clays, after treatment with acids, contain various transition stages between quartz and colloidal silica. The differences in reactivity of these made use of in the attempt to separate them, are of degree only and not of kind, so that the results obtained must depend most intimately on concentration, temperature, time of contact with the extracting solution, etc., and no complete separation can be possible.

The estimation of the colloidal organic matter or "humus" present in soils presents several features of interest and seems to have been put on a pretty sound basis. Reference may be made to two interesting papers on the subject by Beam.[159] The soil is first treated with hydrochloric acid to remove carbonates, etc., and is then washed with either CO_2 water or 0.5 per cent hydrochloric acid so as to avoid complete flocculation of the clay. The humus is then dissolved—peptized—in ammonia and a small amount of clay, which is also peptized, precipitated by means of ammonium carbonate. The filtrate is then evaporated and the residue of humus weighed.

The cementing action of organic colloids tends to make the results of mechanical analyses of peaty soils of little value. Robinson [160] shows that this can be overcome by heating the soil with hydrogen peroxide.

Stannic acid plays an interesting part in two cases of analytical importance which may be mentioned here. In the well known Purple of Cassius test it has been shown [161] that the purple precipitate results from the co-precipitation of sols of gold and stannic acid. The mixed gel is easily peptized by ammonia with formation of a red colloidal solution.

The second case is that of a method which is sometimes used for removing phosphoric acid from solution either with metallic tin and nitric acid or with stannic acid gel.[162] Whichever method of working is used, about 40 times as much SnO_2 is required as there is P_2O_5 to remove, and the process may certainly be classed as adsorptive. The process has been modified recently by Gattermann and Schindhelm,[163] who showed that a freshly prepared cold solution of stannic chloride is an excellent agent for removing phosphoric acid from solution. On boiling, a precipitate, closely approximating to stannic phosphate in composition, is thrown down in a form which is easily filtered while only one gram of SnO_2 is required to remove half a gram of P_2O_5. There seems good reason to regard the precipitate formed in this way as a definite compound, and it is a good instance of the closeness with which the phenomena of adsorption and of ordinary chemical combination are linked together.

Supposed influence of colloidal silicic acid on permanganate titrations.—Schwarz and Rolfes [164] stated that if colloidal silicic acid were used in conjunction with the usual $MnSO_4$, H_3PO_4 mixture, perfect results could be obtained in the titration of ferrous iron in hydrochloric acid solution using permanganate solution standardized by any of the usual methods. This statement led to a lengthy controversy between Schwarz [165] and Brandt.[166] Brandt[167] has now published experiments which show that the addition of pure silicic acid sols prepared from $SiCl_4$ has no inhibiting action on the liberation of small amounts of free chlorine in side reactions and no influence on the results obtained in titrating ferrous chloride with potassium permanganate either in presence or absence of manganese sulphate. Commercial water glass contains oxidizable impurities which tend to cause erratic results when the effect of silicic acid from that source is examined.

Effect of colloidal matter on titrations involving ferric thiocyanate indicator.—The presence of colloidal matter is liable to cause an uncertain endpoint in titrations of chlorides by Volhard's method.[167a] The electrometric method gives satisfactory results in such cases.[167b] The thiocyanate method of determining soil acidity also suffers from a similar disturbance [167c] which is due to the ready hydrolysis of ferric thiocyanate and adsorption of the resulting ferric hydroxide by the colloidal water present.

Radium is liable to be adsorbed by silica unless free acid is present in considerable amount. This may be of importance when estimating the radium present in rocks.[168] Radium and other radioactive substances can actually be concentrated by utilizing this adsorption by silicic acid gel.[169] It is to be noted [170] that the co-precipitation of radium sulphate with barium sulphate is essentially an adsorption process in many cases for, owing to the small concentration, the solubility product of radium sulphate will frequently not be reached. Germann [171] has shown that this adsorption follows the same laws that hold for much stronger solutions even when the solution being experimented with contained only 22.79×10^{-10} grm. radium per c.c.

The molybdenum blue reaction in which a solution of molybdic acid becomes blue on treatment with stannous chloride (or other reducing agents such as mercurous nitrate or metallic zinc) is, according to Feigl [172] a colloidal phenomenon. He considers that the blue color is due to a derivative of $Mo(OH)_5$, possibly its molybdate, in a colloidal form and finds support for this opinion in the fact that the best conditions for the formation of the blue color are, a low acidity, absence of neutral salts and a low temperature. However, the correctness of this view may perhaps be doubted especially as the blue substance dissolves readily in amyl alcohol.

The sudden clearing of a solution as the end point of a titration has been indicated by Sacher [173] in the case of the titration of lead by ammonium molybdate. Colloidal lead molybdate causes a turbidity so long as the reaction is incomplete, but there is a sudden clearance at the end point. As a matter of fact, this kind of behavior is frequently observed to some degree during precipitations, and some well marked instances of it are well known, as for example that of silver iodide.[174]

Electrical precipitation of aqueous colloidal solutions does not appear to have been applied quantitatively, but it has been used for the analysis of smokes by means of a modified Cottrell precipitator by Tolman, Reyerson, Brooks and Smyth.[175]

Drinker, Thomson and Fitchett [176] have discussed the theory of high tension electric precipitation, in connection with the construction and operation of small precipitators for the quantitative determination of smokes, fumes and dusts in air.

Electro-dialysis is coming into use for the purification of colloids. A simple apparatus for the purpose has been described by Fuchs and Housig [176a] while the electrolytic purification of precipitates such as aluminium hydroxide from acidic impurities has been suggested by Charriou.[176b] Quantitative separation of proteins from serum can be conveniently effected by electrodialysis according to Wernicke.[176c]

Colorimetry and nephelometry.—Increasing analytical use is being made of methods where colloidal solutions of highly colored or colorless compounds are intentionally produced and the amount of substance in suspension then determined either colorimetrically or nephelometrically. Protective colloids may be added, if necessary, in order to keep the substance, which is being estimated, in suspension. Well known examples of such methods are the colorimetric method for determining traces of lead as sulphide or the nephelometric method for determining traces of chloride as silver chloride. A history of this method and the development of instruments is given by Kober and Graves,[176a] while some of the essential conditions of illumination, etc., which must be observed have been discussed by Lednicky [177] and Kleinmann.[177a] A new type of nephelometer has been described by Kingslake.[177b] The nephelometry of colored hydrosols has been dealt with by Bechhold and Hebler [178] while the same authors have described the preparation and properties of a standard turbidity and sol of barium sulphate.[179] They have examined nephelometrically the connection between the turbidity and the size of the suspended particles.[180] For suspensions containing the same amount of barium sulphate but of varying degrees of dispersion the turbidity increases from 2.5 μ downwards. The maximum turbidity is reached with particles of about 800 $\mu\mu$ for white light. Further reduction of the size of particles caused the turbidity to decrease strongly.*

When a colored colloid is formed in a reaction its actual color may vary considerably owing to differences in the degree of dispersion quite apart from any ordinary chemical differences. Differences in the color changes passed through in the tyrosinase reaction (production of melanin) are accounted for in this way by Haehn.[181] †

Use of protective colloids in analytical chemistry.—The presence of colloidal organic matter may seriously interfere with ordinary gravimetric analyses owing to the protective action of the colloid keeping precipitates in suspension. With other types of quantitative methods this protective action is not necessarily disadvantageous and may in fact be useful, as already mentioned under the heading Colorimetry and Nephelometry. In some volumetric methods involving precipitation it may also be advantageous to prevent actual coagulation of the precipitate. This is the case when titrating iodides with silver nitrate on account of the marked adsorption of iodide or silver nitrate by coagulated silver iodide. The addition of gum arabic [182] or starch [183] has been recommended for the purpose of keeping the silver iodide in suspension.

The protective action of organic colloids is not likely to interfere with electrometric titrations. Treadwell, Jarrett and Blumenthal [184] have shown that $AgNO_3$ — NaCl can be titrated electrometrically in presence of a protective colloid such as gelatin without appreciable loss of sharpness at the end point. From the titration curve it was calculated that the solubility of the colloidal silver chloride was about 2×10^{-2} milligram mols. per litre which is about twice the solubility of ordinary silver chloride. The colloidal chloride was not found to introduce any error through adsorption of Cl' or $Ag^{\cdot}$ ions though such errors were observed in the titration of silver with a soluble sulphide.

Differentiation between colloidal and non-colloidal forms of the same substance present in admixture.—Various colloidal preparations are nowadays of technical and, more especially, of pharmaceutical importance. It may at times be necessary to distinguish between colloidal and non-colloidal forms of a substance in such materials. Gutbier, Huber and Kuppinger [185] have published a method for estimating ionic silver in preparations of colloidal silver. It depends on the fact that the protected colloidal silver is coagulated by methyl alcohol. The coagulum is liable to carry down silver ion by adsorption, however. For this reason the ionic silver is converted into a complex ion before the coagulation by methyl alcohol, and this is best done by addition of excess of ammonium carbonate. After removal of the coagulated silver, any silver remaining in solution is titrated by Volhard's method. Lottermoser[186] has described a sedimentation method and an optical method, both of which give approximately the same results for the technical estimation of the colloidal part of tungsten powder. Diénert and Wandenbulcke[187] have shown that the colorimetric molybdic method permits of the differentiation of colloidal and non-colloidal silica. The latter is the form which normally occurs in waters.

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* Consider also the color variations of iron oxide and of lead chromate with degree of dispersion. J. A.

† In the determination of albumin in urine by opalescence, turbidity, cloud or nephelometric methods, such factors as protectors, p_H, electrolyte concentration, etc., may seriously affect the size of the dispersed particles and hence the accuracy of the work. J. A.

Influence of colloids on overvoltage.—It is well known that the presence of small amounts of organic colloids, such as gelatin or gum arabic, in the electrolyte sometimes exerts a favorable influence on the character of electrolytic deposits of metals. Use is sometimes made of this technically, but, so far as the writer is aware, colloidal additions are not ever made in any of the electrolytic methods of analysis. When such additions are made organic colloidal matter is apt to be deposited along with the metal which would of course be bad for analytical purposes.

The effects produced by such colloid additions are probably due to the formation of complex ions between the sol particles and the metal ions or the hydrogen ions also present. The effect of gelatin on the discharge potential of hydrogen has been investigated by Izgaryschev and Berkmann.[188] With increase in the gelatin concentration, the discharge potential rises to a maximum and then falls. In small amounts at least, the presence of gelatin thus renders the liberation of hydrogen more difficult. Indications were also obtained of the formation of complexes between gelatin and zinc ions.[189] Even sucrose appears to form complexes with zinc[190] and this is of some interest in view of the fact that sugar is often added to keep lead sulphide in suspension when traces of lead are estimated colorimetrically. Sugar also appears to exercise a definite peptizing effect on colloidal gold.[191] Silver ions and gelatin also form complexes according to Audubert,[192] who found by E.M.F. measurements that the concentration of silver ions was reduced on addition of gelatin to a solution of silver nitrate.

Indicators[193] are liable to be removed from solution owing to adsorption by any fiber or precipitate present. Difficulty is seldom or ever likely to be experienced from this cause, however. Very serious trouble of another kind may, however, be encountered when using indicators which themselves have colloidal properties. This type of indicator, of which congo red is one of the best known, is usually colloidal in the sense of forming alkali salts which are colloidal electrolytes and yield colloidal negative ions. The color changes shown by such indicators can be explained in purely colloidal terms, for the color will depend on the dispersion of the sol, which itself depends on the hydrogen ion concentration. Thus congo red in acid solution forms larger particles than in alkaline solution and is blue, in conformity with Ostwald's rule that increase in the size of particles shifts the color towards the blue end of the spectrum. Similarly neutral salts also tend to give the blue color and this effect increases with the valency of the cation, in agreement with Schulze's rule. With $Ba(OH)_2$ the color remains blue since the influence of the $Ba^{\cdot\cdot}$ ion is greater than that of the OH'. In presence of other colloids congo red may yield results which are absolutely erroneous. Emulsoids such as casein, gelatin, etc., exert a protective action and tend to prevent the formation of larger particles and the color change to blue. Most indicators are effected to some extent by organic colloids, especially by proteins, those of a relatively simple structure being as a rule least affected. Owing to this action indicators which are to be used in presence of proteins, as in much physiological work, must be carefully selected from among those having little tendency to become colloidal and showing little or no "protein error." The "protein error" must be supposed to be due to a disturbance of the normal indicator equilibria owing to the formation of a proportion of colloidal indicator under the influence of the protein or alternatively to the formation of a colloidal salt or adsorption complex of protein and indicator. Only in extreme cases could the simple colloidal explanation given above for congo red by Weigner [194] be considered adequate. It must not be supposed that the generally accepted ionic theory of indicators can be dispensed with, though it is clear that the colloidal behavior of the indicator may have to be considered. In certain cases this may be even more important than the ionic behavior.

Ultrafiltration by means of collodion membrane filters has been worked out as an analytical operation by Zsigmondy and co-workers,[195] and appears to be useful in some cases, as in blood analysis.[196] * The process should at any rate be of service in studying the mechanism of precipitation. Thus it was found [197] necessary to wait 24 hours before filtering a colloidal solution of barium sulphate, to allow of complete precipitation from the supersaturated solution. This indicates that the usual precautions observed in estimating barium sulphate are not alone required for allowing the particles of the precipitate time to grow to such a size as not to pass through the filter paper.

Fricke and Klempt [198] have described a simple method of preparing ultra filters with cellulose acetate.

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Membrane Filters and Their Uses

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A long-needed desideratum is a filter permitting rapid filtration, whose pore-size is intermediate between that of the slow-acting clay filters and collodion ultra-filters. In collaboration with Dr. W. Bachmann I have produced such filters and they have surpassed all expectations; for not only do they permit rapid filtration, but they can be prepared in a wide variety of pore-sizes, so that they may be used for a large number of purposes. The new filters we call *Membrane Filters,*[1] and their chief characteristics are the following:

(1) The filters are parchment-like, smooth and white, have polished surfaces, and are impermeable to all ordinary analytical precipitates; the coarser ones retain all microscopic particles, the finer ones retain ultramicrons as well.

(2) Tested bacteria filters positively retain bacteria, and are furthermore not proliferated by bacteria.[2]

(3) The smooth surface of the filter permits of a thorough removal of precipitates, as if from glazed paper, so that the filters may be successfully used in quantitative analysis.[3]

The filters are now being made in quantity,[4] and have been widely used in Germany, but are still so little known elsewhere that a description of them is not out of place here. They are made of nitro-cellulose, like collodion ultrafilters, but unlike these, may be dried without losing their porosity. They are about 0.2-0.3 mm. thick, reasonably strong, are easily handled, and may be used in a variety of apparatus.

Membrane filters are made by a patented process, by pouring out on plates solutions of nitrocellulose in two appropriate solvents, *e.g.,* acetone and glacial acetic acid, and then drying in a stream of air of predetermined moisture content; the amount of moisture in the air controls the size of the pores. The surface energy and the eddies due to it, act like a loom producing a fabric, but no man-made mechanism can produce such an ultramicroscopically fine structure. This natural "machine" can be set to do finer or coarser work, just as we can control the size of stitches in a sewing machine, and even although we do not know exactly its exact mechanism.

Apparatus

In preparing chemical substances and in analytical chemistry the Zsigmondy filtration apparatus[6] is preferably used; this consists of a glass funnel, a large porcelain perforated filter plate, on which is placed a glass ring. Larger and smaller units and similar apparatus may be used.[7]

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* Translated by Gertrude E. Alexander, B.L.

For bacteriological use the apparatus is preferably made of bronze to facilitate sterilization by steam. Various sizes are made.[7]

With very impervious filters and with difficultly filterable colloidal solutions it is necessary to use high pressure to secure filtration. Apparatus that will stand a pressure of 100 atmospheres (1500 pounds per sq. in.), and which has given good results in my laboratory, are made by Sartorius-Overke, in Goettingen.[7] Furthermore, there are various other kinds of apparatus for filtration under pressure while being stirred by electric power; these have given good results in my laboratory with albumin, serum and dye filtrations, for they permit the colloidally dissolved material to be speedily and completely separated.

For clarifying water, a small immersion apparatus[8] is most suitable, as I have also found out by experiment.

Testing Membrane Filters

Membrane filters may be tested in several ways: we may determine the speed of filtration of 100 cc. of water against a vacuum, using an instrument of the first type with a filter surface of 80 square centimeters. Coarse pored filters allow 100 cc. to pass in 1 to 5 seconds, medium pored in from 10 to 30 seconds, fine pored in from 35 to 100 seconds, while with the finest pored filters it takes still longer.

To find imperfections and to estimate the maximum pore size of filters to be used for bacteriological purposes, air under pressure is used. This method, first developed by Bechhold, detects imperfections with certainty, and permits of an approximate estimation of the pore size.[2] As Meyeringh has shown,[2] filters which do not permit the passage of air-bells, under a pressure of 4 atmospheres are impervious to bacteria. Their maximum pore size is under 0.75 μ.

Membrane filters may also be used for the approximate estimation of the size of colloid particles, but must first be gauged with gold or graphite hydrosols of known particle size. In gauging it is necessary to reduce as far as possible the adsorption of the gold particles by the filter, by protecting the gold hydrosol[9] (*e.g.*, AuF) by traces of alkali or gum arabic.[9a] Once the pore size of the filter is approximately known, we may estimate the particle size of other hydrosols, even if their particles[10] cannot be made ultramicroscopically visible.

Application in Analytical Chemistry

As previously stated, precipitates may be quantitatively removed from membrane filters, like a powder from glazed paper. In colloboration with G. Jander a method was developed,[3] which, when one gets the knack, is of great advantage in analytical chemistry, because gelatinous precipitates which readily pass through filter paper, are completely held back by membrane filters. Furthermore, membrane filters save time in that filtration and the washing of precipitates can be done in less time and with less fluid than by usual methods. Jander[3] and his pupils have worked out a series of applications, also suitable for quick multiple analyses.

Application to Bacteriology and Water-clarification

Membrane filters have found many applications in bacteriology, medicine, serology, etc.[11] Thus as Ficker[12] has shown, bacteria are readily separated from their toxins, much better than with the filter candles commonly used. H. Citron[13] reports the demonstration of tuberculosis bacilli.

The previously mentioned work of Meyeringh is of the utmost importance in the filtration of drinking water; he proved that filtration through a tested membrane filter completely removes pathogenic bacteria, and that the bacteria cannot grow through the filter. [This may not apply to "filter-passers"—see Vol. II. J. A.]

With the aid of the immersion apparatus above referred to, I have myself tested numerous waters and have found that many natural waters, especially swamp waters, and also brook and river water, and in fewer cases the tap water of cities, contain very variable amounts of slimy material, which clings to the surface of the membrane filter, covering it with a film very difficult to pass. These filters can therefore be used advantageously to test water for heretofore unsuspected slimes, as I have shown in one of my communications.[14] The same may also be said of my new apparatus for water purification,[8] and this gives a method of removing slimes from water *so that rapid filtration for clarifying drinking water is possible.*

From these brief remarks on membrane filters, it may be seen not only that this new filter material has manifold uses, but also that these uses have been found. It is to be hoped that they will have the widespread use that is warranted by their quality; and they are so little known outside of Germany only because conditions there make impossible the expense of widespread propaganda.

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